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The Journal
of the
Society of Dyers and Colourists

Volume 77 Number 12

SCIENCE AND CRAFT IN BOTH TEXTILE AND NON-TEXTILE COLORATION

Proceedings of a Symposium held at Bristol
on 20th, 21st, and 22nd September 1961

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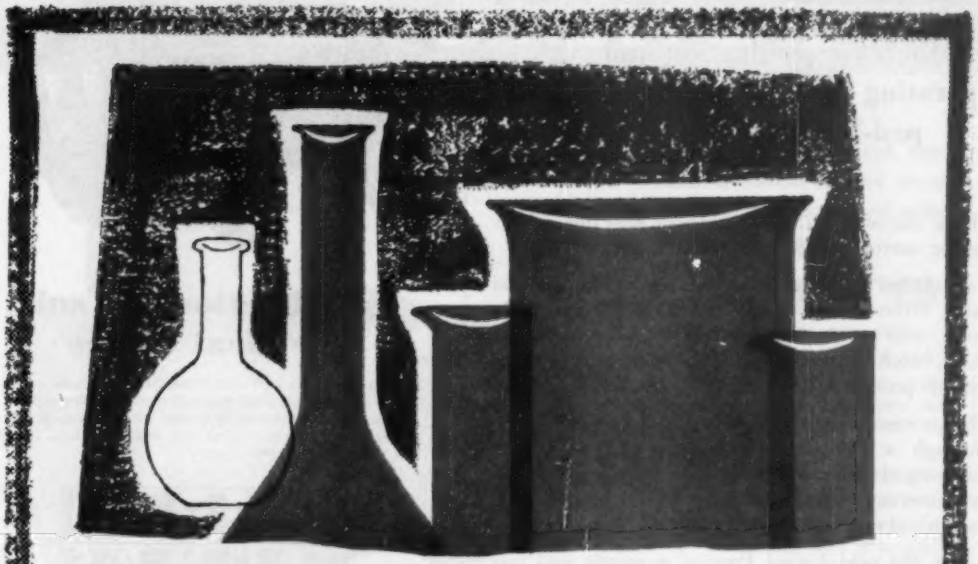

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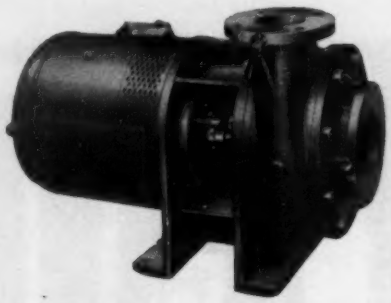

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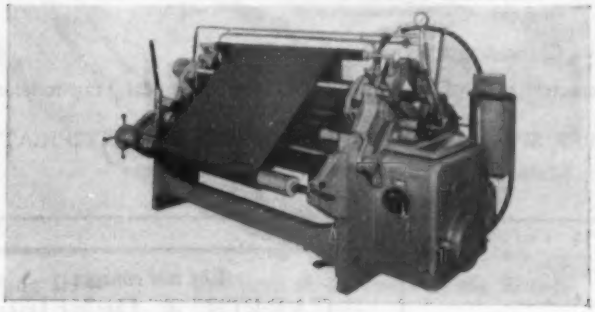

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(Abstracts section only—see January issue, page 2)

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Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1–8 of the January 1961 and pages 277–285 of the July 1961 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Scouring and Dyeing Blends for the Carpet Trade — *R. C. Cheetham*

Dyeing and Finishing Terylene–Linen Fabrics — *I. E. Haden*

The Problem of Illumination in Colour Matching — *K. McLaren*

Some Fundamental Aspects of the Washing Process — *G. J. Parish*

Combined Dyeing and Finishing of Cellulosic Piece Goods — *I. D. Rattee*

An Introduction to Organic Pigments — *F. M. Smith*

COMMUNICATIONS

The State of Indigoid and Thioindigoid Dyes in Dyed Materials — *G. S. Egerton and F. Galil*

Two Problems associated with the Blending of Coloured Fibres — *J. C. Guthrie, (Miss) J. Moir and P. H. Oliver*

Photochemistry of Sodium Chlorite in Solution, with special reference to Chlorite Bleaching — *C. Kujirai and I. Fujita*

Sorption of Acids by Wool from Mixtures of the Acids
I— Sorption of Hydrochloric Acid and Dichloroacetic Acid or Monochloroacetic Acid — *P. Larose and R. Donovan*

Paper Chromatography of Insoluble Dyes — *J. Sramek*

Characterisation of Solvent-soluble Dyes by Optical Transmission Methods — *I. F. Trotter*

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Identification of Reactive Dyes on Cellulosic Fibres — *F. Jordinson and R. Lockwood*

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Volume 77 Number 12 DECEMBER 1961 Issued Monthly

Science and Craft in Both Textile and Non-textile Coloration

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Symposium Activities

Some 200 delegates, including a number from the Continent, attended the Society's ninth Symposium. One of the outstanding features of the technical programme was the use of the Eidophor colour television system in the presentation of four of the papers, namely those by Peters and White; Alderson, Atherton, and Derbyshire; Bell; and Whittaker. In addition, Ciba Clayton Ltd, who generously made the equipment available, arranged two special lectures which revealed the potentialities and the versatility of this system of colour television. Dr. Hans Traber of Zürich, a leading microscopist, demonstrated the appearance under the microscope of single-cell animals and plants and certain multi-cell creatures. In the other lecture Professor S. Tolansky of the University of London described the study of surfaces by microtopography and the use of contour maps. These two lectures admirably demonstrated how valuable scientific information can be obtained by making a mountain out of a molehill.

The social side of the Symposium also played an important part. On Tuesday evening the President and Mrs. Hannay held an informal reception, at which there was dancing, in the Ballroom Suite of the Grand Hotel. On the following evening most of the delegates and their wives attended a reception given by the Lord Mayor of Bristol and the Lady Mayoress at the Council House. The Symposium Dinner and Dance was held on Friday evening; the speeches are reported on the following pages.

In addition to these functions, visits were made to Wells Cathedral and Glastonbury, and to the Severn Wild Fowl Trust and Berkeley Castle. By courtesy of Messrs J. Harvey & Co., a wine tasting was held on the Thursday evening, and later that evening many delegates visited the Theatre Royal, the oldest theatre in England.

The amenities of the Ashton Court Country Club were placed at the disposal of delegates, who were also able to use the facilities of the Long Ashton, Bristol and Clifton, and Henbury Golf Clubs. The ladies were not forgotten, since Messrs J. F. Taylor & Son Ltd. made available to them tickets for fashion shows held in their show-rooms.

Opening of the Symposium

Wednesday, 20th September 1961 at 9.30 a.m.

The Symposium was formally opened by the President of the Society (Mr. RAMSAY J. HANNAY).

Mr. HANNAY said that the decision to meet in Bristol was due to a desire to give encouragement to the newly formed West of England and South Wales Section of the Society, in which there were many enthusiastic workers. The Bristol area contained an amazing variety of industries and it was because of this that the programme included, in addition to papers on the coloration of textiles, lectures on the coloration of plastics and leather, and on coloristic aspects of paper and paint. The breadth of the subject matter emphasised the Society's concern with the art and science of coloration of all types of substrates.

Symposium Dinner

The Symposium Dinner and Dance was held on Friday, 22nd September 1961, under the presidency of Mr. Ramsay J. Hannay.

"THE CITY AND COUNTY OF BRISTOL"

After the toast of "Her Majesty the Queen", that of "The City and County of Bristol" was proposed by—

Mr. F. M. STEVENSON, J.P. (*Immediate Past President of the Society*), who said that everyone was conscious that the men of Bristol had played a vital part in making England great in times gone by. They had explored continents and founded colonies in the pursuit of the ideals of peace. They had carried to the ends of the earth the products of the country's craftsmen. Equally, they had played their part in time of war. From Bristol went the ships carrying men who were to be the forerunners of our civilisation, and in recent times Bristol had borne the brunt of enemy attack with fortitude.

Visitors to Bristol found imposing buildings and prosperous manufacturing units. Members of the Society in particular were impressed by the coloration of its buildings; Bristol seemed to have preserved the beauty of contour and perfection of colour that aroused the envy of those from less favoured areas.

At the Reception given by the Lord Mayor at the Council House, they had gained further knowledge of the city's history and treasures. They were impressed by the courtesy with which they had been received and the spirit of adventure which they sensed. When the Society decided to establish the West of England and South Wales Section two years ago, it took a step for which it would never be sorry.

Alderman CHARLES H. SMITH (*The Lord Mayor of Bristol*), who responded to the toast, re-emphasised the welcome that the city had given at the Reception on Wednesday evening. He had every reason to believe that they had felt intense satisfaction from their discussions that week. The Society had shown initiative in illustrating lectures by means of a colour television unit, and he had watched the Eidophor demonstration film, "Seeing the Very Small", with great interest.

Bristolians were extremely proud of their city and were determined that this pride should not be misplaced. They welcomed the fact that the Council of the Society had the foresight to recognise the importance of Bristol and to establish a Section there. The Society had an opportunity of serving the public in a way that the average person had not; the *Colour Index*, in particular, was held in high regard by industry.

The city that was "virtuous and industrious" had taken them to its heart; he hoped that at some future date the Symposium would again be held in Bristol.

"THE SOCIETY OF DYERS AND COLOURISTS"

Professor WILSON BAKER, F.R.S. (*Professor of Organic Chemistry, University of Bristol*) proposed the toast of "The Society of Dyers and Colourists".

He referred to the development of the industry from the accidental discovery of the first synthetic dye by William Henry Perkin in 1856, and of the diazo reaction by Peter Griess a few years later which led to the introduction of azo dyes. It had been stated that since then over one million compounds had been produced as potential dyes, but only about 3,500 had been found of practical value. The world's dyemakers were said to spend £300 million a year on research.

From the 1880s to the 1930s a course in dye chemistry was an integral part of a university honours degree in chemistry, but this was no longer the case. Today many students were woefully ignorant of dye chemistry because no longer was there time in a three-year course to include it. Because of this situation, the dye-making and dye-using industries must be failing to attract many good people to their ranks. Professor Baker felt that the monthly *Journal* of the Society, which had appeared regularly since 1884, and the *Colour Index*— the "Encyclopaedia Britannica of the colour industry"— were not as well known as they should be. He suggested that the Society might consider making its *Journal* available to university libraries, since this would, he felt sure, result in the recruitment of highly qualified organic chemists by the dyestuff industry.

Mr. RAMSAY J. HANNAY (*President of the Society*), responding, said he had received from Mr. John Boulton, President of the International Federation of Associations of Textile Chemists and

Colourists, and a past President of the Society, a message of good wishes from the Federation.

The Society was very conscious of the work being done in the universities; copies of the *Journal* were already made available to certain universities and technical colleges. He, personally, felt that one of the advantages of a university course was that it provided a wider background against which to apply a technology later, whatever it might be.

The Society had chosen Bristol for this year's Symposium because it was the centre of their youngest Section. The Society had something to offer to industry and to the young people going into industry; they also had a tradition to maintain. Their meetings were held in a very friendly atmosphere that encouraged the exchange of ideas and knowledge.

The Society received excellent support from industry, and if they could encourage the industries in the Bristol area to give the same support that they received elsewhere, they would have done the job they set out to do.

"OUR GUESTS"

Mr. R. C. OAKLEY, O.St.J. (*President-elect of the Society*) proposing the toast to the guests, said that the Symposium in Bristol would long be remembered, not only for its valuable contribution to the work of the Society, but also for the warm hospitality that they had received from the City. Thanks had already been expressed for this hospitality and to those who had contributed in many ways to the pleasure of delegates and the success of the Symposium.

The Society therefore welcomed the opportunity to have many ladies and gentlemen as honoured guests on such a festive occasion, made all the more so by the Lord Mayor's sharing his birthday with them. He welcomed the guests and thanked them for the honour and pleasure of their company.

Mr. J. PITTARD (*President, British Leather Manufacturers' Research Association*) responded for the guests.

Speaking of the *Colour Index*, he said that he was first introduced to it in 1927. The second edition of the *Colour Index*, published in 1956, was a masterpiece when one realised the rate at which new dyes and pigments were being produced; the amount of work involved in the attempt to collate all the information possible was tremendous. Its value was recognised all over the world; 50 sets had just been sent to Russia.

The work of the Society was done by dedicated people, and the best traditions of the art and craft of coloration had been maintained. The success of the forum in Bristol was an illustration of the valuable work that was being done. The dissemination of knowledge by the various speakers and the frank discussions and arguments which followed could do nothing but good to the industry as a whole.

Britain today had nothing to sell but the skill of her people; British skill could help to ensure that we maintained our position in the world as a great trading nation.

WEDNESDAY MORNING, 20th SEPTEMBER 1961

Chairman— Mr. RAMSAY J. HANNAY

The Effect of Heat-setting Treatments on the Dyeing Behaviour of Nylon Yarns and Fabrics

H. W. PETERS and T. R. WHITE

The effects of dry-heat setting and pressure-steam setting on the dyeing behaviour of nylon yarns are considered. Measurements have been made of the influence of the temperature and duration of dry-heat setting on the rates of dyeing of nylon 6.6 yarns and fabrics with the direct dye Chlorazol Violet R (C.I. Direct Violet 3) and the 1:2 metal-complex dyes Irgalan Red 3G (C.I. Acid Red 220) and Irgalan Grey BL (C.I. Acid Black 58). Similar measurements were carried out on steam-set nylon 6.6 yarns to examine the influence of presteaming conditions, steam pressure, steam quality, and variation of the steam-setting procedure. The practical implications of the results are discussed, especially with regard to uniform setting and subsequent dyeing behaviour of nylon yarns and fabrics. The effects of dry-heat and pressure-steam setting are interpreted in terms of the proposed molecular mechanism of setting, which considers especially the influence of moisture on the fine structure of nylon.

Introduction

All polyamide yarns and fabrics are subjected to some form of heat treatment to confer dimensional stability and desirable textile properties. Heat treatment or setting of fabrics can be carried out by several methods [1–3]. Only the principles of four widely used methods will be mentioned here.

(*a*) *Hot-air setting* This is the most common method; it has the advantages of a continuous process. The fabrics are held at open width on a pin stenter and heated in an enclosure by jets of hot air, usually at 195–225°C (380–440°F). Exposure time depends to some extent on the fabric weight but is usually 15–30 s.

(*b*) *Radiant-heat* (*infrared*) *setting* This is also carried out on a pin stenter, but the temperature of the cloth is raised by the selective absorption by the fibre of infrared radiation emitted from electrically heated sheathed wire elements.

(*c*) *Hot rolling or calendering* This is a very efficient way of raising the fabric temperature and, being a continuous method, is economically attractive, but there is very little control of fabric width.

(*d*) *Pressure-steam setting* This is practised at present as a batch process. The fabric is batched and set in steam, at pressures up to about 40 lb/in^2 gauge, in an autoclave. This produces a fabric with a soft handle and good crease resistance, but there is no control of width.

Supply yarns are often subjected to heat treatments. For example, a stable filament crimp is necessary to give cohesion and bulk to yarn for processing into worsted-type staple, and the dimensional and mechanical properties of the crimped filament are effectively stabilised by setting in saturated steam under pressure. Steam setting of crimped nylon tow for pile fabrics is necessary to impart desirable fabric handle; dry-heat setting gives a limp, inferior pile. Twist-setting of nylon carpet yarns in steam is carried out to give desirable texturised effects [4]. Within the past few years bulked continuous-filament yarns have been developed on a considerable scale. The production of bulked yarns by false-twist processes generally involves the use of dry-heat setting carried out on the threadline immediately after twisting. Heat treatments of the type described have long been known to affect the dyeing behaviour of nylon yarns, and inadequate control of the processes to lead to unevenly dyed fabrics [4–7].

The amount of anionic dye absorbed and the rate of dyeing depend on the concentration of amine end-groups [8–10]. Changes in the degree of order or crystallinity of the polyamide and in the degree of orientation of both the ordered regions and the molecular chains in amorphous regions influence the behaviour toward many dyes [11, 12]. Heat-setting treatments alter the physical fine structure of polyamide yarns, and hot-air setting also results in a decrease in amine end-group content through oxidation. The effect of heat-setting on dyeing with a particular dye will depend on the sensitivity of the dye to physical and chemical variations in nylon yarns [13]. The uptake of the acid triphenylmethane dye Kiton Pure Blue V (C.I. Acid Blue 1) has been used to determine the setting effect produced by steam on nylon 6 yarns [14].

More detailed information has recently become available on the effect of both dry-heat setting and pressure-steam setting on the dyeing behaviour of nylon 6.6 [15, 16] and nylon 6 [15, 17–22] yarns. The results of published work show that dry-heat setting of polyamide fabrics at temperatures of up to about 200°C causes a decrease in the equilibrium uptake and rate of dyeing for all the classes of dyes investigated. Results obtained at H.A.T.R.A.[16] showed that the rate of dyeing with Cibalan Blue BRL (C.I. Acid Blue 170) of false-twist nylon 6.6 yarns set by dry heat decreased to a minimum at heater temperatures of 200–210°C and then rose rapidly at higher heater temperatures until the uptake of yarn heat-set at about 250°C exceeded that of the flat unprocessed yarn. A similar effect was noted with nylon 6.6 fabric set by dry heat in an experimental fluidised bed. Setting in saturated steam generally increases the rate of dyeing of nylon yarns. The results obtained in all

the published work emphasise the difficulties that can be caused in fabric dyeing by non-uniform heat setting.

The work described in this paper is aimed at obtaining information on the heat-setting variables that have practical significance for the dimensional, mechanical, and dyeing properties of nylon 6.6 yarns. The programme is by no means complete, but sufficient information is now available, together with the published results of other workers, to enable a reasonable guide to the important factors in the heat-setting of nylon yarns to be presented.

The observations on the effects of heat-setting treatments on the dyeing behaviour of nylon yarns have wider implications with regard to the fine structure of polyamides and the effects of heat and moisture on the structure. The results therefore have both an immediate practical value and a theoretical significance which will be briefly discussed.

Experimental

Except where otherwise stated, experiments were carried out on nylon 6.6 yarns of 6 denier per filament.

Dye content of fibre was determined by the absorptiometry of phenol–water solutions of the fibre dyed under standard conditions. Relative dyeing rates were determined from measurements of dye uptake after a standard time.

EFFECT OF SETTING TREATMENTS ON EQUILIBRIUM MOISTURE REGAIN AND DYE UPTAKE

The effects of dry-heat setting for 5 min in air at 200°C and setting in steam under 25 lb/in² gauge pressure on the uptake of the direct cotton dye Chlorazol Violet R (C.I. Direct Violet 3) and the 1:2 metal-complex dye Irgalan Red 3G (C.I. Acid Red 220) by nylon 6.6 yarns are shown in Fig. 1, in which the dye uptake is expressed in arbitrary units. The results illustrate that dry-heat setting at 200°C decreased both the equilibrium uptake and the rate of dyeing with both dyes. Steam setting had little or no effect on the equilibrium dye uptake of Chlorazol Violet R, but the value for Irgalan Red 3G was increased slightly. The rate of dyeing was increased in both cases.

The percentage moisture regains of the control and heat-set yarns are given in Table I.

TABLE I

Effect of Setting on Moisture Regain of Nylon 6.6 Yarns

Setting treatment	Moisture regain at 20°C and 65% r.h. (%)
None	4·02
Air 200°C, 5 min	2·98
Steam 25 lb/in² gauge pressure, 5 min	4·17

DRY-HEAT SETTING OF NYLON 6.6 YARNS

Effect on Amine End-group Content

Oxidative degradation occurs fairly rapidly when yarns of nylon 6 or 6.6 are heated in air at temperatures above about 200°C; prolonged heating at lower temperatures (e.g. 150°C) also results in oxidation. This oxidation is characterised by breakage of polymer chains, an increase in carboxyl end-group content, and a decrease in amine end-group content.

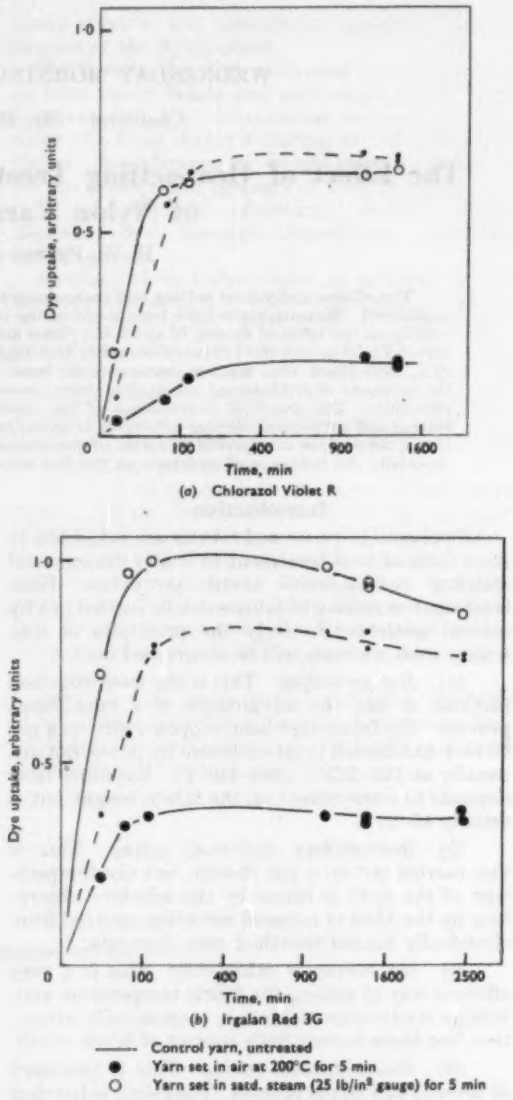

FIG. 1— Effect of setting on the uptake of dyes by nylon 6.6 yarns

Fig. 2 shows the decrease in amine end-group (AEG) content, determined as described by Price[23], for 15-den. monofil, Type 100 and 30/10* Type 100 yarns exposed in air at 215°C (ca. 420°F) for up to 60 s. The results confirm previous findings that the decrease in AEG on heating normal nylon 6.6 yarns in air is independent of filament denier.

Fig. 3 shows the changes in AEG content that occurred when a locknit fabric constructed from 40/13/½Z†, Type 100 yarn was set on a stenter frame

* 30-Denier, 10-filament.

† For details of designations of yarn structure see T.T.S. No. 62, *J. Textile Inst.*, 51, P87 (1960).

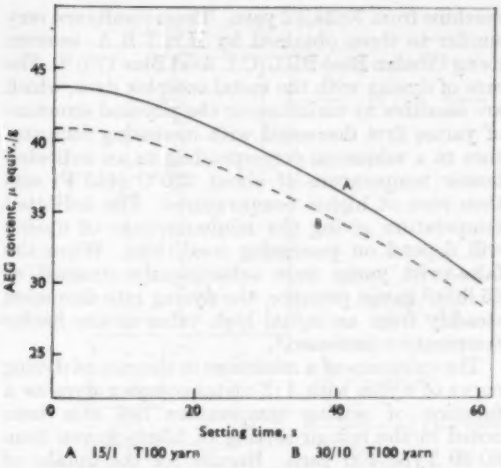

FIG. 2— Effect of setting time in air at 215°C on amine end-group (AEG) content of nylon 6.6 yarns

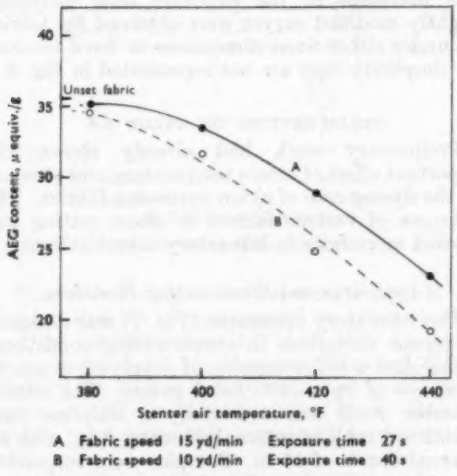

FIG. 3— Effect of stenter dry-heat setting on AEG content of locknit nylon 6.6 fabric

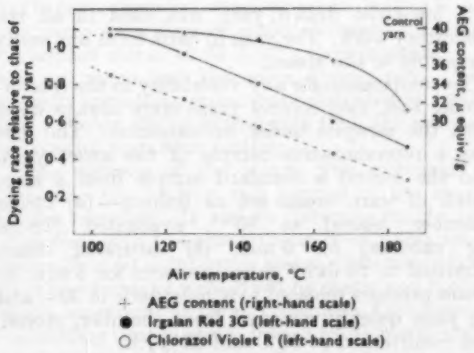

FIG. 4— Effect of heating in air for 5 min on dyeing rate and AEG content of nylon 6.6 yarns

in hot air at 380–440°F (ca. 193–227°C) and at fabric speeds of 10 and 15 yd/min, giving exposure times of 40 and 27 s, respectively.

Changes in AEG content of yarns heated for 5 min at 100–185°C are shown in Fig. 4.

These results illustrate the marked decrease in AEG content that occurs when nylon 6.6 is heated in air at high temperatures or for fairly long times.

Effect on Dyeing

Samples of the locknit fabrics set on the hot-air stenter together with samples of the grey scoured and steam-set (25 lb/in² gauge) fabrics, were dyed with the following dyes.

(*a*) 1% Durazol Blue 2R (C.I. Direct Blue 71), at the boil. This dye is very sensitive to both physical and chemical variations in nylon yarns.

(*b*) 1% Solway Blue BN (C.I. Acid Blue 45), at the boil. This dye is sensitive to chemical variation but relatively insensitive to variations in physical structure.

(*c*) 1% Irgalan Grey BL (C.I. Acid Black 58), at the boil. This is a neutral-dyeing 1:2 metal-complex dye which is very sensitive to physical variations but only slightly sensitive to chemical variations.

(*d*) 2% Duranol Brilliant Blue BN (C.I. Disperse Blue 3), at 60 and 85°C. At 85°C this disperse dye is insensitive to both physical and chemical variations in nylon yarns but at 60°C it becomes sensitive to variations in physical structure.

Each series was visually examined for depth of dyeing and for stripiness. The overall picture which emerged was as follows.

Dry-heat setting with stenter air temperatures up to about 440°F (ca. 227°C) reduced the rate of dyeing relative to that of the unset fabric with dyes sensitive to physical variations in yarn and with dyes sensitive to amine end-group content.

The assessment of the dyed fabrics is rendered difficult by differences in depth of dyeing between the pieces; however, with the very sensitive dyes chosen to accentuate the variations the overall pattern of stripiness remains the same.

Laboratory measurements of rates of dyeing with Chlorazol Violet R and Irgalan Red 3G were used to determine the effects of heating for 5 min in air or nitrogen at 100–185°C. The standardised determinations of rate of dyeing, based on measurements of the optical density of phenol–water solutions of the dyed yarns will not be detailed here. The results, expressed as dye content (or rate of dyeing) of the set yarn relative to that of the unset control yarn are shown in Fig. 4, together with AEG values for the yarns heated in air. They illustrate the marked drop in rate of dyeing of nylon yarns on heating in air at 120–185°C.

The effect on the absorption of 1:2 metal-complex dyes of heating nylon 6.6 yarns in air at temperatures approaching the melting point (265°C) is illustrated in Fig. 5, which shows the rate of absorption of Irgalan Grey BL by false-twist crimped yarns processed on a Scragg CS2

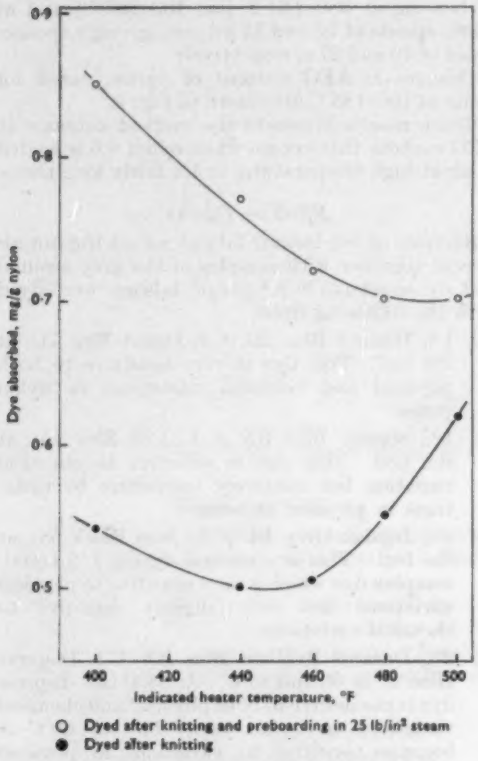

FIG. 5— Effect of twist-setting temperature on rate of absorption of Irgalan Grey BL by false-twist crimped nylon 6.6

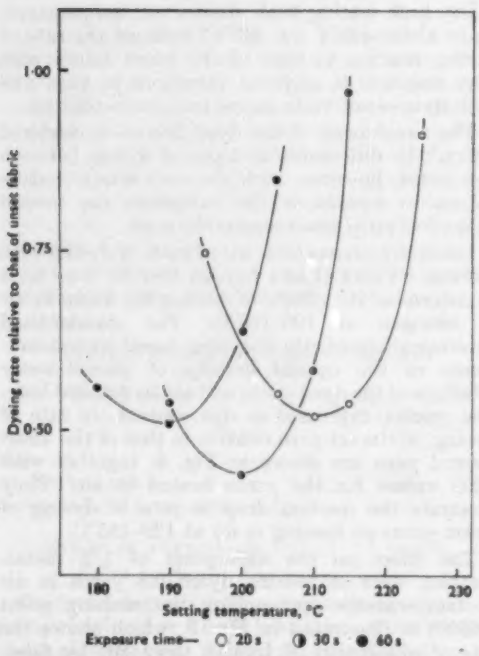

FIG. 6— Effect of dry-heat setting temperature on rate of absorption of Irgalan Grey BL by nylon 6.6 fabric

machine from 70/34/½Z yarn. These results are very similar to those obtained by H.A.T.R.A. workers using Cibalan Blue BRL (C.I. Acid Blue 170)[16]. The rate of dyeing with the metal-complex dyes, which are sensitive to variations in the physical structure of yarns, first decreased with increasing temperature to a minimum corresponding to an indicated heater temperature of about 230°C (445°F) and then rose at higher temperatures. The indicated temperature giving the minimum rate of dyeing will depend on processing conditions. When the false-twist yarns were subsequently steamed at 25 lb/in² gauge pressure, the dyeing rate decreased steadily from an initial high value as the heater temperature increased*.

The existence of a minimum in the rate of dyeing curve of nylon with 1:2 metal-complex dyes as a function of setting temperature has also been noted in the hot-air setting of fabric woven from 60/20 Type 100 yarn. Results for the uptake of Irgalan Grey BL by fabric set under relaxed conditions in air at 180–225°C with exposure times of 20, 30, or 60 s are given in Fig. 6. The setting temperature giving the minimum dyeing rate decreases as the exposure time increases. Slightly modified curves were obtained for fabrics set under either fixed dimensions or fixed tension; for simplicity they are not represented in Fig. 6.

STEAM-SETTING OF NYLON 6.6

Preliminary work had already shown the important effect of steam temperature and pressure on the dyeing rate of nylon yarns and fabrics. The influence of various factors in steam setting was studied more fully in laboratory investigations.

Apparatus and Steam-setting Procedure

The laboratory apparatus (Fig. 7) was designed to permit variations in steam-setting conditions. It included a boiler capable of supplying steam at pressures of up to 100 lb/in² gauge. The setting chamber itself was essentially a stainless steel cylindrical tank of internal diameter 6 in. with an internal depth of 15 in. Samples were suspended from the quick-release lid which was fitted with a calibrated Rototherm thermometer. Superheated steam was obtained by the combined operation of a throttle valve and an electrically heated superheater coil.

A low-twist drawn yarn was used in all the laboratory work. The yarn in hank form was easily accessible to the steam.

To compensate for any variability in the rate-of-dyeing test, two control yarns were always dyed with the samples under investigation. The first was a representative sample of the unset yarn, and the second a standard sample from a large batch of yarn steam-set as follows— (*a*) steam chamber heated at 80°C, evacuated (75-cm Hg vacuum) for 5 min, (*b*) saturated steam admitted to 25 lb/in² gauge pressure for 5 min, (*c*) steam pressure released to atmospheric in 30 s, and (*d*) yarn quickly removed from chamber, stored, and conditioned at 20°C and 65% r.h.

* Further work has shown this statement to be incorrect— see Discussion, first contribution by Mr. Jaeckel and authors' reply.

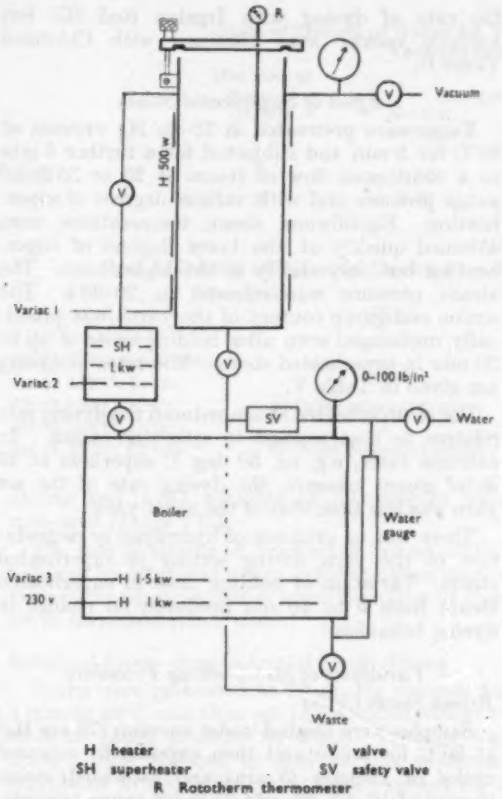

FIG. 7— Steam-setting apparatus

Rates of dyeing with Chlorazol Violet R and Irgalan Red 3G were measured on triplicate 0·1-g samples conditioned at 20°C and 65% r.h. before being scoured in 1% aqueous Dispersol VL at 65–70°C for 30 min and equilibrated in de-ionised water at 85°C just before being dyed. Relative dyeing rates have been expressed to the nearest 0·05.

Effects of Water Content of Yarn and Steam and of Holding Time in Steam

Yarns were pre-treated for 3 days at room temperatures under conditions varying from a P_2O_5-dry evacuated atmosphere to 90% r.h. and the yarns were then set under standard conditions (saturated steam at 25 lb/in² gauge pressure). All the set yarns had the same dyeing rate. Yarn actually containing an excess of water before setting had a higher (20%) dyeing rate than the standard set control yarn after setting.

The wetness of the steam was increased by removing the heating and lagging of the steam-setting chamber. It had no influence on the rate of dyeing with Chlorazol Violet R of yarns set in either 25 or 50 lb/in² gauge steam. Identical effects on rates of dyeing were given by static and flowing steam conditions at given pressures. Variations of the holding time in steam from 2 to 30 min at either gauge pressure had no significant influence on the dyeing rate.

Effect of Preheat Conditions

Preheat Temperature and Preheating Time

The effect was investigated of preheating yarns for 5 min at 60–120°C under 75-cm Hg vacuum, and then setting for a further 5 min in saturated steam of 25 lb/in² gauge pressure, the steam pressure being reduced to atmospheric within 20–30 s. The dyeing rates were measured relative to that of yarn pretreated at 80°C in 75-cm Hg vacuum for 5 min and set in saturated steam at a gauge pressure of 25 lb/in² for a further 5 min. Results are given in Table II.

TABLE II

Effect of Preheat Temperature on Rate of Dyeing of Steam-set Nylon 6.6 Yarns

Preheat temp. (°C) (75-cm Hg vacuum)	Relative rate of dyeing in Chlorazol Violet R	Irgalan Red 3G
60	1·05	1·00
80	1·00	1·00
100	0·90	0·95
110	0·85	0·90
120	0·70	0·80

Preheat temperature has a marked influence on the dyeing rate of steam-set nylon yarn, increase in preheat temperature giving a decreased dyeing rate; the effect is more marked for Chlorazol Violet R than for Irgalan Red 3G.

Variation of preheating time from 3 to 30 min at a given preheat temperature had no significant influence on dyeing rates.

Residual Air in Steam-setting Chamber

The work on hot-air setting of nylon yarns had shown that the dyeing rate can be reduced by heating in air even at temperatures as low as 100°C. Incomplete evacuation of a steam-setting cabinet may therefore result in a lower rate of dyeing than would otherwise have been obtained. The effects of residual air in the steam-setting cabinet and of preheating temperatures were therefore investigated.

A series of experiments was carried out in which air was deliberately left in the cabinet by using different degrees of evacuation before admitting steam to give a total pressure of 25 lb/in² gauge. In one case air under a pressure of 10 lb/in² gauge was introduced. A preheat temperature of 110°C was used with a holding time of 3 min before introduction of the steam. Table III lists the rates of dyeing of the set yarns with Chlorazol Violet R relative to that of the standard steam-set control yarn.

TABLE III

Effect of Residual Air in Steam-setting on Dyeing Rate of Nylon 6.6 Yarns

Residual air pressure (cm Hg)	Steam temp. (°C)	Relative rate of dyeing with Chlorazol Violet R
1·5	130	0·85
15	128	0·75
45	126	0·65
125	121	0·50
Unset yarn		0·25

Incomplete evacuation of the steam-setting cabinet during preheating results in a lower maximum steam-setting temperature and a reduction in the rate of dyeing of the steam-set yarns.

Effect of Saturated Steam Pressure

Samples of yarn were set in saturated flowing steam at pressures of up to 60 lb/in² gauge. Preheat conditions were 80°C for 5 min under 75-cm Hg vacuum, and the steam pressure was reduced to atmospheric in 30 s. Only slight changes in amine end-group content were produced by steam setting (Table IV).

TABLE IV
AEG Content of Steam-set Yarns

Steam pressure (lb/in²)	AEG (μ equiv/g)
0	39·8
25	39·7
35	39·6
50	39·5
60	39·1

The slight decrease with increased pressure is probably due to slight oxidation at higher temperatures caused by residual air (ca. 1-cm Hg pressure) in the steam chamber.

The effects of the pressure of the saturated steam on the rate of dyeing are shown in Fig. 8. The trends for Chlorazol Violet R and Irgalan Red 3G are almost identical. Yarn set at 50 lb/in² gauge attained 85% saturation with Chlorazol Violet R after dyeing for 1 h at 85°C.

Variation in the rate of release of steam pressure and in the time allowed for the apparatus to cool to zero gauge pressure had very little effect on the rate of dyeing with Irgalan Red 3G, but variable results were obtained with Chlorazol Violet R.

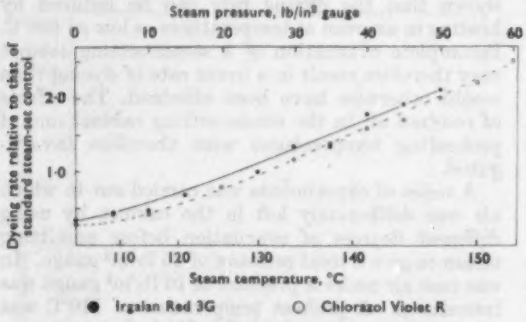

FIG. 8—Effect of pressure of saturated steam on rate of dyeing of nylon 6.6 yarns

Effect of Superheated Steam

Yarns were pretreated in 75-cm Hg vacuum at 80°C for 5 min and subjected for a further 5 min to a continuous flow of steam at 25 or 35 lb/in² gauge pressure and with various degrees of superheating. Equilibrium steam temperatures were attained quickly at the lower degrees of superheating but only slowly at the higher ones. The steam pressure was released in 20–30 s. The amine end-group content of the yarns was practically unchanged even after holding times of up to 30 min in superheated steam. The rates of dyeing are given in Table V.

Use of superheated steam reduced the dyeing rate relative to that realised in saturated steam. In extreme cases, e.g. ca. 50 deg. C superheat at 25 lb/in² steam pressure, the dyeing rate of the set yarn was less than that of the unset yarn.

There was no evidence of hydrolysis or degradation of the yarn during setting in superheated steam. Variation of holding time in superheated steam from 5 to 30 min produced no change in dyeing behaviour.

Variations of Steam-setting Procedure

Repeat Steam Cycles

Samples were treated under vacuum (75-cm Hg) at 80°C for 5 min and then exposed to repeated cycles of vacuum (5 min) and saturated steam (5 min) of 10, 15, 20, and 25 lb/in² gauge pressure, followed by pressure release over 20–30 s. Further samples were similarly treated in steam pressure cycles of 10, 20, 30, and 35 lb/in². All the yarns were then conditioned and the rates of dyeing with Chlorazol Violet R measured (Table VI).

Yarns to which steam is freely accessible have, when set in repeated cycles of vacuum and pressure steam, a lower rate of dyeing than when set by a single treatment in steam at the maximum pressure.

Hot Air–Saturated Steam Setting

Skeins of yarn were set for 5 and 15 min in air at 130°C, then subjected to the standard heat-setting treatment of 5 min preheat under vacuum (75-cm Hg) at 80°C and 5 min in saturated steam at 25 lb/in² gauge. After conditioning, the rates of

TABLE V
Effect of Superheated Steam on Rate of Dyeing of Nylon 6.6 Yarn

Steam properties			Relative rate of dyeing of yarn with	
Pressure (lb/in² gauge)	Temp. (°C)	Deg. C superheat	Chlorazol Violet R	Irgalan Red 3G
25	130	0	1·00	1·00
	132	2	0·90	0·85
	150	20	0·35	0·30
	185	55	0·25	—
	205	75	—	0·30
35	138	0	1·35	—
	150	12	0·55	—
	173	35	0·35	—
Unset yarn			0·30	0·35

TABLE VI

Rate of Dyeing of Nylon 6.6 Yarns Set under Repeated Cycles of Vacuum and Pressure-steam

Max. steam pressure (lb/in²)	Relative rate of dyeing (compared with standard steam-set control)		
	Normal setting	Repeated cycles at lb/in² 10, 15, 20, 25	Repeated cycles at lb/in² 10, 20, 30, 35
25	1·00	0·85	—
35	1·35	—	1·15

TABLE VII

Rate of Dyeing of Nylon 6.6 Drawn Yarn Heated in Air and then Set in Saturated Steam

Treatment (I)	Treatment (II)	AEG (μ equiv/g)	Relative rate of dyeing with Chlorazol Violet R	Relative rate of dyeing with Irgalan Red 3G
None		39·8	0·30	0·35
25 lb/in² saturated steam	—	39·7	1·00	1·00
Air at 130°C, 5 min	—	39·5	0·20	0·30
Air at 130°C, 5 min	25 lb/in² saturated steam	39·3	0·95	0·85
Air at 130°C, 15 min	—	38·8	0·15	0·25
Air at 130°C, 15 min	25 lb/in² saturated steam	38·3	0·90	0·80

dyeing and AEG contents of all samples were measured (Table VII).

The rate of dyeing of yarn set in air at 130°C, followed by saturated steam, is greater than that of yarn set in air alone, but is lower than that of yarn set in saturated steam alone.

Saturated Steam–Supersaturated Steam Setting

Yarns were preheated at 75-cm Hg vacuum for 5 min at 80°C and then set in saturated steam at 25 lb/in² gauge pressure for 5 min. Pressure was then quickly reduced to give various superheat conditions to which the yarns were exposed for a further 2 min before pressure was released completely.

Further samples were preheated as before, and then exposed for 2 min to superheated steam at 5 lb/in² gauge pressure and various degrees of superheat. Finally, the yarns were subjected to saturated steam at 25 lb/in² gauge pressure for 5 min before the pressure was reduced to atmospheric over 20–30 s.

The samples were conditioned and the rates of dyeing with Chlorazol Violet R (Table VIII) and Irgalan Red 3G (Table IX) measured.

Treatment of nylon yarn in superheated steam after setting in saturated steam results in the rate of dyeing being decreased relative to that of yarn set in saturated steam only.

Discussion and Conclusion

GENERAL

The measurements of dyeing rate were intended to be relevant to dye uptake in the early stages of normal commercial dyeing, the dyes chosen being especially sensitive to differences in physical structure. These results obtained with nylon 6.6 yarns have been combined with published data on both nylon 6 and nylon 6.6 to give the summary (Fig. 9) illustrating the general influence of temperature of setting in air or saturated steam on the rate of dyeing with acid, disperse, and neutral-dyeing metal-complex dyes. Nylon 6 melts at 220–230°C and the portions of the dry-heat-setting curves at higher temperatures refer only to nylon 6.6. Notable general features of the results are—

(*a*) the difference in the effects produced by dry heat, e.g. hot air or superheated steam, on the

TABLE VIII

Rate of Dyeing of Set Nylon 6.6 Yarns with Chlorazol Violet R

Setting treatment (I)	Setting treatment (II)	Relative dyeing rate
25 lb/in² saturated steam, 5 min	—	1·00
25 lb/in² saturated steam, 2 min	25 lb/in² saturated steam, 5 min	1·00
25 lb/in² saturated steam, 5 min	5 lb/in² steam, 2 deg. C superheat, 2 min	0·90
25 lb/in² saturated steam, 5 min	5 lb/in² steam, 14 deg. C superheat, 2 min	0·75
5 lb/in² steam, 7 deg. C superheat, 2 min	25 lb/in² saturated steam, 5 min	1·00
5 lb/in² steam, 10 deg. C superheat, 2 min	25 lb/in² saturated steam, 5 min	1·00

TABLE IX

Rate of Dyeing of Set Nylon 6.6 Yarns with Irgalan Red 3G

Setting treatment (I)	Setting treatment (II)	Relative dyeing rate
25 lb/in² saturated steam, 5 min	—	1·00
25 lb/in² saturated steam, 5 min	14 lb/in² steam, 1 deg. C superheat, 2 min	0·90
25 lb/in² saturated steam, 5 min	9 lb/in² steam, 2 deg. C superheat, 2 min	0·85
25 lb/in² saturated steam, 5 min	6 lb/in² steam, 6 deg. C superheat, 2 min	0·85

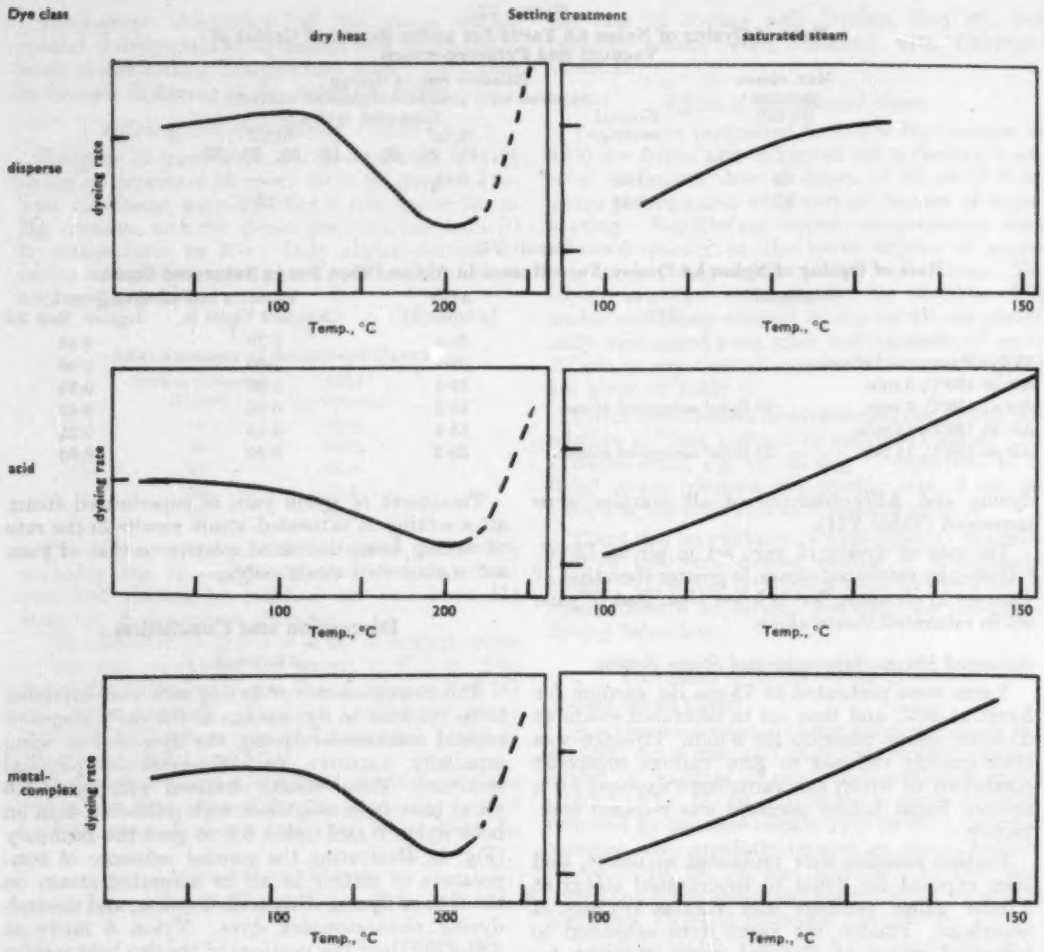

FIG. 9— Effect of setting on rate of dyeing of nylon yarns

one hand and saturated steam on the other, and

(*b*) the similar effects produced by a particular heat-setting process on the rates of dyeing with all three classes of dye.

The actual effects produced in a particular heat-setting process will depend on the conditions of heat transfer and steam penetration; tensions developed in the yarn during setting will also have an influence, tending to reduce dyeing rates. The yarns in the present experiments were steam-set under relaxed conditions with free access of steam.

Heating in air results in a decrease in the equilibrium uptake of acid, disperse, and metal-complex dyes. The dyeing rate generally decreases to a minimum at setting temperatures of about 200°C. Heating above about 200°C results in the dyeing rate increasing again. At these temperatures there is an increasing tendency for structural changes to occur before actual fusion of the polyamide.

Setting in saturated steam increases the dyeing rate with the three classes of dyes; the effect with acid and metal-complex dyes is proportional to steam pressure or is proportionately greater at higher temperatures, whilst with disperse dyes the effect is greatest at the lower steam temperatures. Steam setting has little or no effect on the equilibrium uptake of acid dyes. The slight reductions noted are probably due to the small decrease in amine end-group content through oxidation by small quantities of residual air in the steam-setting vessel. We do not agree with the conclusions of the Japanese workers[17–19] that the decrease in equilibrium acid dye uptake is caused by a masking effect on amine end-groups by additional crystallisation induced by the setting treatment. The equilibrium uptake of metal-complex dyes is increased slightly by setting in saturated steam.

Superheated steam reduces the dyeing rate and has been classed with dry heat or heated liquid metals as giving non-swelling heat-setting conditions[7].

If a given heat-setting treatment alters the equilibrium uptake of a dye, then differences in

TABLE X

Effect of Setting on the Dyeing Behaviour of Nylon Yarns

Dye class	Hot-air setting (dry heat)			Saturated-steam setting		
	C_∞	R_d	D	C_∞	R_d	D
Acid	decrease	decrease	decrease	little or no change	increase	increase
Disperse	decrease	decrease	decrease	increase	increase	—
Metal-complex	decrease	decrease	slight increase	slight increase	increase	increase

dyeing caused by variations in heat setting cannot be eliminated by prolonged dyeing. Although theoretically it should be possible to obtain level dyeing of yarns which differ only in rates of dyeing, in commercial practice this may not be feasible. Table X summarises the effects of hot-air (180–200°C) and saturated-steam (e.g., 25 lb/in² gauge) setting on the equilibrium uptake (C_∞), rate of dye uptake (R_d), and diffusion coefficient within the fibre (D) for the three classes of dye.

Steam setting not only confers stable dimensional and mechanical properties on nylon yarns and fabrics; it increases the dyeing rates and does not degrade or discolour the nylon. It is, however, currently more difficult to carry out than dry-heat setting and gives no control over fabric dimensions.

A temperature of 130°C has been suggested as the optimum temperature for setting in steam and temperatures of 190 ± 2°C and 225 ± 8°C for dry-heat setting of nylon 6 and 6.6, respectively [7].

PRACTICAL IMPLICATIONS

Dry-heat Setting in Air

The main points of practical importance may be summarised.

1. Heating nylon yarns or fabrics under normal industrial conditions (180–220°C for nylon 6.6 fabrics or 200–230°C for false-twist processes) causes an appreciable decrease in dyeing rate and of amine end-group content. Variation of 1 deg. C in setting temperature can produce differences of about 1% in dyeing rate. Control of setting temperature, setting time, and heat-transfer conditions are especially important. These are obviously important points to consider in machine design.

2. Prolonged heating at 110–140°C, temperatures often used for drying yarns and fabrics, causes appreciable differences in dyeing rate. The effects are noticeable for heating times of 5 min.

3. Although dry-heat setting alters the dyeing rate and equilibrium uptake, the general level of stripiness in a fabric dyed with sensitive dyes remains unaltered. This is independent of whether or not the original stripiness is due to chemical or physical differences in the yarn.

Steam Setting

Steam setting in a cabinet in fact consists in a dry-heat setting during preheating and evacuation and a wet-heat setting on introduction of saturated (or wet) steam. If subsequent conditions cause the steam to become superheated (or dry), the effects of another dry-heat setting are introduced. Variations in the efficacies of the two types of setting can therefore produce marked variations in dyeing properties.

The main factors that appear likely to cause dyeing differences are discussed below.

Preheat Conditions

1. Although the wetness of the steam or the moisture content of the yarn has little or no effect, the presence of excess of water in the material has the same effect on dyeing rate as steam setting at a temperature 10 deg. C higher. Materials should therefore not be wet in patches before being set.

2. Preheating before steam setting lowers the dyeing rate but is necessary to prevent excessive condensation of steam and is inevitable with large cabinets in continual use. It is desirable to aim at a fixed preheat temperature.

3. The presence of residual air in the setting cabinet is the most common cause of deficiencies in the physical properties of yarn and fabric [4, 24]. It lowers the setting temperature and causes oxidation; both effects give a lower dyeing rate than would otherwise have been produced. The adverse effects of residual air in pressure-steam cabinets in reducing the ultimate steam temperature at a given pressure, prolonging the time taken to reach this temperature, causing temperature variations within the cabinet, adversely affecting steam penetration into packages, and decreasing the rate of heat transfer to materials in the cabinet, have been usefully discussed in a monograph on the sterilisation of surgical materials [25]. Fourné has suggested [7] that the maximum permissible oxygen concentration in the steam during setting should be 1%.

Steaming Conditions

1. Dyeing rate increases linearly with pressure; a three-fold increase in dyeing rate is produced by setting in steam of 25 lb/in² gauge. The rate of increase of dyeing rate is about 4% per lb/in² or 5% per deg. C. Significant differences in depth of dyeing of set nylon yarns and fabrics can be produced by differences of 2 lb/in² in the pressure of saturated steam. The importance of accurate temperature control during steam setting has been emphasised by several authors [4, 15, 16].

2. Superheated steam markedly reduces dyeing rate, and any conditions liable to give uneven superheating, e.g. rapid release of pressure with continued high temperature, can easily lead to uneven dyeing throughout a batch.

3. Uniform penetration of steam into a fairly large batch of material presents difficulties. Procedures using repeated steaming cycles with the precaution of temperature recording at the centre of the load have been described [4, 7].

These considerations emphasise the need to ensure that all commercial heat treatments of nylon yarns and fabrics are controlled and kept as uniform as possible.

POLYAMIDE STRUCTURE AND THE MECHANISM OF DYE DIFFUSION

The physical structure generally accepted for polyamides is that of a semi-crystalline solid in which the ordered regions are composed of parallel segments of polyamide chains held together through hydrogen bonding or electrostatic interaction between the amide groups [28]. Amorphous regions are composed of randomly disposed segments of the polyamide chains which are capable of a considerable degree of rotation unless they interact with one another. Portions of a given polyamide chain may be involved in three-dimensional order in crystalline regions whilst other portions pass through less well-ordered and completely amorphous regions. Intermediate states of order between crystalline and completely amorphous regions with randomly directed molecular chains are believed to exist [28]. In these intermediate states of order the chains may be parallel over a considerable portion of their length, but each molecule can have any orientation around the chain axis and this orientation need not be related in any way to that of neighbouring chains. In this discussion the term "order" is used to denote the extent to which parts of the polyamide chains lie parallel to and interact with one another to give a repeated sequence of molecular structure. When molecular structure sequences are reproduced in three dimensions the material is a true crystal.

The cold-drawing process results in a slight reduction in moisture regain [29, 22] (e.g., 4·5 to 4·3% for nylon 6.6 at room temp. and 65% r.h.), which would imply an increase in degree of total order although the overall density is only slightly increased [30, 31]. This is probably explained by the increase in crystallinity and formation of voids during cold-drawing [29].

Irreversible dimensional changes in cold-drawn polyamide yarns occur on heating or treatment with swelling agents [22, 23]. These treatments would tend to weaken amide–amide interactions and permit increased rotation of chain segments. Movement of chain molecules in the completely amorphous and partially ordered regions would occur to give randomly disposed chains and the system would tend to a state of lower free energy. On cooling or removal of the swelling treatment, new amide–amide interactions may be formed [9b, 33]. The density of cold-drawn nylon filaments is increased by dry-heat treatment or steam setting [15, 22].

The amount of moisture sorbed by polyamides at a given temperature increases with relative humidity [34–36]. This sorption is assumed to occur at free amide sites in the amorphous regions, and the extent of sorption is believed to be proportional to the amorphous content of the polymer [30, 32, 37]. The crystalline regions are generally believed to be inaccessible to moisture.

It has been calculated that only 6% of the amide groups of normal cold-drawn nylon 6.6 are available as sorption sites for water [38]. The remainder are bound to other amide groups. From evidence of the moisture sorption, density, and swelling properties of nylon 6.6 filaments, it has been calculated that 65% of the total fibre is non-crystalline and 12% of the fibre volume occupied by the non-crystalline region may be considered to be voids [30]. The fact that the greater proportion of space in nylon 6.6 filaments remains inaccessible to moisture even in saturated humidities led to speculation of possible arrangements of molecular chains which, without having a crystalline configuration, are unavailable as sorption sites for small molecules or result in effective barriers to diffusion.

There are no reliable data available for the moisture content of nylon fibres in pressure-steam. Parks [39] has quoted a moisture content of 7·54% for nylon 6.6 yarn in steam at atmospheric pressure. Jeffries [40] concluded from his results at 120°C and 150°C that there is a decrease in moisture sorbed by nylon 6.6 yarns in steam with increase in saturated steam temperature (and therefore pressure), but it is not clear whether the large increase in steam density with temperature has been taken into account in calculating the results.

Nylon yarn set in dry heat behaves differently in dyeing from yarn set in saturated steam or in hot water. A similar effect on phenol sorption has been observed [22, 33] and it has been concluded that during dry-heat setting the molecular chains assume configurations that are different from those obtained when molecules of water are present. Pokrovskiĭ and Pakshver [22] concluded that the significant difference in macrostructure of steamed nylon 6 was due to the breakdown of an oriented skin and the formation of molecular pores. Their results show an increased overall density for nylon 6 steam-set at 140°C, but they assumed the development of porosity and decreased density in amorphous regions.

We have summarised in Table XI the effects of heating in air and in saturated steam on some properties relevant to the fine structure of nylon 6 and 6.6 yarns; the section dealing with the effect of dry heat at 250°C applies only to nylon 6.6. The

TABLE XI

Effect of Setting Treatment on Properties of Cold-drawn Nylon Yarns

Yarn property	Heating in air		Heating in saturated steam
	180–220°C	240–250°C (nylon 6.6)	
AEG concn.	decrease	decrease	little or no change
density	increase	increase	increase
moisture regain	decrease	decrease	increase
phenol sorption	decrease	decrease	increase
optical birefringence	increase	decrease	decrease
crystallinity (X-ray)	increase	—	increase
orientation (X-ray)	decrease	decrease	decrease

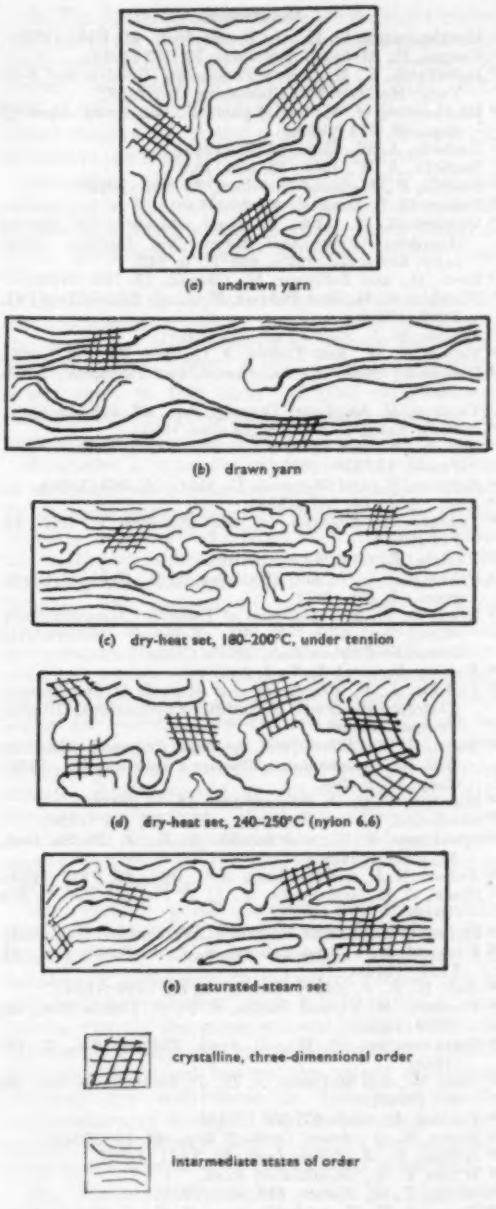
(a) undrawn yarn
(b) drawn yarn
(c) dry-heat set, 180–200°C, under tension
(d) dry-heat set, 240–250°C (nylon 6.6)
(e) saturated-steam set
crystalline, three-dimensional order
intermediate states of order

FIG. 10—Schematic representation of fine structure of nylon yarns

differences in the properties listed in the table again indicate that different physical structures are produced in the yarn by the two types of heat setting.

Consideration of these effects lead us to propose that the fine structure of polyamide yarns may be represented as shown in Fig. 10. The undrawn yarn (Fig. 10*a*) consists of approx. 30% crystalline material and about 5% completely amorphous material, the remainder having intermediate states of order. All the structural units are randomly disposed. Cold-drawing results in the alignment of the structural units along the fibre axis with the creation of voids. A slight decrease in crystallinity occurs but there is an increase in the proportion of material having intermediate states of order (Fig. 10*b*). On being heat set in air at temperatures around 200°C the polyamide chains attain increased mobility. At temperatures above 140°C moisture is rapidly desorbed from the polyamide [41] and the formation of new amide–amide interactions can occur comparatively unhindered by the presence of water molecules when the segments of two parallel chains come into close proximity. In this way a slight increase in the total order in the structure occurs and the number of amide groups available for the sorption of water, phenol, etc. is diminished. At temperatures of about 200°C the rotational energy of molecular segments not bonded to one another is sufficient to permit the chains to attain a random coil configuration having the lowest entropy state, and this will introduce contractive forces in the structure. At the same time this temperature is not sufficiently high to cause extensive rupture of the partly and fully ordered regions. The result is a slight increase in orientation of the ordered regions with disorientation of the amorphous regions (Fig. 10*c*) when the fibre is under tension during dry-heat setting.

At higher temperatures, the partly ordered regions undergo a form of melting, but the dissociated molecular chains rapidly form stable crystal structures. In this transition, disorientation occurs. The occurrence of two distinct thermal transitions in the melting process of drawn yarns of many of the crystalline polymers has been previously reported [42]. The resultant structure is represented in Fig. 10*d*.

In the case of steam setting we consider that increased amounts of water penetrate the yarn as the steam pressure increases. The linear relation between rate of dye uptake for both acid and metal-complex dyes and saturated steam pressure suggests that the change in physical structure is proportional to the moisture content of the yarn, which we would expect to be proportional to steam pressure. The combined effect of temperature and presence of water molecules increasingly breaks up the regions with only low degrees of order, and a high proportion of polymer chains attains random coil configuration, causing a decrease in volume, elimination of voids, and marked disorientation of the amorphous regions. At the same time there is an increase in the amount of crystalline material and a decrease in the orientation of the crystalline regions. The presence of large quantities of sorbed water prevents the newly formed "amorphous" regions associating to give partly ordered structures. The type of structure envisaged is represented diagrammatically in Fig. 10*e*. At steam pressures of about 90–100 lb/in^2 gauge, nylon 6.6 fuses at 165–170°C, which is about 100 deg. C below the normal melting range.

In superheated (or unsaturated) steam the yarn will lose moisture to the atmosphere and the effect attained will then tend towards that given by dry-heat setting. We would thus expect the

effects of saturated and superheated steam to be reversible and the final effect to depend mainly on the final treatment given to the fibre. This is borne out by the results given in Tables VIII and IX.

The sorption sites for disperse dyes are believed to be the available amide groups [9c]. These dyes are sensitive to the degree of order but generally insensitive to orientation [11, 12, 15]. Disperse dyes cannot easily penetrate spherulitic regions, and there is an inverse relation between the uptake of Duranol Brilliant Blue BN (C.I. Disperse Blue 3) and the visible spherulite content. Annealing undrawn nylon yarn at 230°C causes a decrease in uptake of this dye, but there may be no detectable change in number, size, or character of the visible spherulitic regions, and X-ray analysis does not reveal any increase in the extent of three-dimensional crystalline order [42]. This could be explained by the increase in the intermediate states of order. The effects of dry-heat and steam setting of nylon yarns on the uptake of disperse dyes (Table X) are in keeping with the view that free amide groups provide the final dyeing sites and are concerned in dye-transfer mechanism.

The sorption of anionic dyes is largely governed by the concentration of amine end-groups, but the amide groups are thought also to be involved when "over-dyeing" conditions are employed. The effects of dry heat (air and superheated steam) and saturated steam can be explained if it is assumed that both the number of available amide groups and the degree of orientation control the diffusion of these dyes.

Rough calculations, using the data of Fig. 1, of the effect of heat setting on the diffusion coefficient of the 1:2 metal-complex dye within the fibre indicated that it was increased after both heat-setting treatments. This isolated result is somewhat surprising for dry-heat setting and requires further investigation. We are currently investigating the mechanism of the dyeing of nylon with pre-metallised dyes; Zollinger has already published several papers on this topic and it is clear that several mechanisms may be involved.

* * *

Much of the experimental work in this paper was carried out by our colleagues, Dr. M. C. Cobb, Mr. S. C. Cox, Mr. M. V. Forward, and Mr. R. L. Jones.

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References

1 Mecklenburgh, G. K., *J. Textile Inst.*, **41**, P161 (1950).
2 Fourné, F., *Melliand Textilber.*, **33**, 753 (1952).
3 Inderfurth, K. H., *Nylon Technology* (London and New York: McGraw–Hill Publishing Co., 1953).
4 Richardson, G. M., and Lynch, J. W., *Amer. Dyestuff Rep.*, **47**, 617 (1958).
5 Etchells, A. W., *ibid.*, **35**, 38 (1946).
6 Etchells, A. W., *ibid.*, **40**, 598 (1951).
7 Fourné, F., *Melliand Textilber.*, **33**, 639 (1952).
8 Peters, R. H., *J.S.D.C.*, **61**, 95 (1945).
9 Vickerstaff, T., *The Physical Chemistry of Dyeing* (London: Oliver and Boyd, 2nd Edition, 1954) (*a*) p. 451 *et seq.*, (*b*) p. 440, (*c*) p. 442.
10 Back, G., and Zollinger, H., *Chimia*, **13**, 100 (1959).
11 Munden, A. R., and Palmer, H. J., *J. Textile Inst.*, **41**, P609 (1950).
12 Palmer, H. J., *J.S.D.C.*, **67**, 609 (1951).
13 Peters, H. W., and Turner, J. C., *ibid.*, **74**, 252 (1958).
14 Lauckner, (Miss) A., *Faserforsch. und Textiltech.*, **7**, 124 (1956).
15 Truslow, N. A., *Amer. Dyestuff Rep.*, **47**, 853 (1958).
16 *Hosiery Research Bull.*, **5**, 11 (Jan 1961).
17 Yasuda, T., and Sato, Y., *J. Soc. Textile Cellulose Ind. Japan*, **13**, 338 (1957).
18 Shimizu, T., and Miyaoka, U., *ibid.*, **14**, 563 (1958).
19 *Idem.*, *ibid.*, **14**, 637 (1958).
20 Tsuruta, M., Koshimo, A., and Maehara, T., *ibid.*, **16**, 215 (1960).
21 Yasuda, T., *ibid.*, **17**, 55 (1961).
22 Pokrovskii, L. I., and Pakshver, A. B., *Tekhnol. tekstil. prom.*, **5**, 121 (1959).
23 Price, G. F., in *Techniques of Polymer Characterisation*, edited by Allen, P. W. (London: Butterworths Scientific Publications, 1959), Chap. 7.
24 *Hosiery Research Bull.*, **4**, 2 (1958).
25 Perkins, J. J., *Principles and Methods of Sterilisation.* (Oxford: Blackwell Scientific Publications, Illinois; Thomas Books).
26 Bunn, C. W., *Fibres from Synthetic Polymers*, edited by Hill, R. (Amsterdam: Elsevier Publishing Co., 1953), Chap. 11, p. 290.
27 Slichter, W. P., *J. Polymer Sci.*, **35**, 77 (1959).
28 Sandeman, I., and Keller, A., *ibid.*, **19**, 401 (1956).
29 Speakman, J. B., and Saville, A. K., *J. Textile Inst.*, **37**, P271 (1946).
30 Abbott, N. J., and Goodings, A. C., *ibid.*, **40**, P232 (1949).
31 Black, C. E., and Doyle, M. J., *J. Polymer Sci.*, **3**, 358 (1948).
32 McLaren, A. D., and Rowen, J. W., *ibid.*, **7**, 289 (1951).
33 Forward, M. V., and Palmer, H. J., *J. Textile Inst.*, **45**, T510 (1954).
34 Bull, H. B., *J. Amer. Chem. Soc.*, **66**, 1499 (1944).
35 Forward, M. V., and Smith, S. T., *J. Textile Inst.*, **46**, T158 (1955).
36 Starkweather, H. W., *J. Appl. Polymer Sci.*, **2**, 129 (1959).
37 Dole, M., and McLaren, A. D., *J. Amer. Chem. Soc.*, **69**, 651 (1947).
38 Pauling, L., *ibid.*, **67**, 555 (1945).
39 Parks, W. G., *Amer. Dyestuff Rep.*, **40**, 14 (1951).
40 Jeffries, R., *J. Textile Inst.*, **51**, T441 (1960).
41 White, T. R., unpublished work.
42 White, T. R., *Nature*, **175**, 895 (1955).
43 Forward, M. V., and Simmens, S. C., *J. Textile Inst.*, **46**, T671 (1955).

Discussion

Mr. S. M. JAECKEL: My colleague Mr. D. A. Bampton and I at the Hosiery and Allied Trades Research Association (HATRA) have been working on similar lines for some years, and the authors have indeed mentioned some of our work on p. 601 (Nov 1958; published Jan 1961) and in reference 16. More recent work was disclosed by us in a lecture delivered to the Midlands Section of the Society on April 13th.

In view of our work we should like to comment on the paper. Our results, although on the whole similar qualitatively, differ in several ways quantitatively from those of the BNS workers. We used different dyes and different dyeing conditions, so that it is not surprising that somewhat different results were obtained. However, mention of the differences is, we feel, important, as a warning of the dangers of generalising quantitatively from one dye to another.

I shall comment briefly on the false-twist dry-heat-setting work, Mr. Bampton will comment on the steam-setting work, and I shall follow with a short final remark.

In Fig. 5, the minima on the lower false-twisted-only curve are dependent on processing conditions; BNS used Irgalan Grey BL and a Scragg CS2 heater; we used 2% of Cibalan Blue BRL (C.I. Acid Blue 170) (dyed at 60°C for 1 h at a liquor ratio of 44 : 1) and a Scragg CS1 heater: our minimum is rather lower than the authors'.

Secondly, absolute values of dye uptake, according to Fig. 5, are very different, those found at HATRA being about 20 times those found at BNS, presumably under different dyeing conditions.

Thirdly, the dye uptake ranges found at HATRA are much greater: where temperature overlaps in the work are fairly complete, i.e. in the region 198–250°C (388–482°F), if the dye uptake at 250°C is put equal to 100, then the BNS range (lower, false-twist-only curve, Fig. 5) is 10%, whereas the lowest range found at HATRA [16] is 26%.

Fourthly, a most important point. The effect of steaming after false-twisting (cf. higher curve, fig. 5) under our conditions is definitely *not* a steady decrease in dye uptake from an initial high value as the false-twist heater temperature rises. Of the steaming temperatures used by us after false-twisting, the nearest to the authors' 25 lb/in² (=130·4°C) is 126°C. In this region of steaming temperature both we and the present authors obtained higher dye uptakes after steaming, but we found the dye uptake after steaming to be much higher for material false-twisted at 250°C than for material false-twisted at 198°C, unlike the results in the paper, but more in accord with the relevant samples demonstrated at the Symposium. Our dyeings were separate; if we dye differently false-twisted but similarly steamed samples together, we expect, and find, even bigger differences, owing to competition effects.

One further point deserves stressing: under certain conditions of dyeing, with nearly complete exhaustion in separate dyeings, identical dye uptakes on differently false-twisted fabrics can be achieved: nevertheless, such fabric samples, containing exactly the same amount of dye, still look different, owing to physical optical effects. Although steaming lessens the visual difference, certainly for differences in false-twist heater temperatures of 50 deg. C, and frequently for much smaller differences, e.g. of 5 deg. C, the improvement is not adequate for commercial purposes.

Mr. PETERS: We agree with Mr. Jaeckel's statement about the minimum in dye uptake obtained after steaming. Further work at BNS indicates that there is a minimum for all classes of dye; this minimum varies from dye to dye.

We also have noticed that fabric samples containing the same amount of dye may look different and think the fact is of sufficient importance to warrant further investigation.

Mr. D. A. BAMPTON: There are three comments on the steaming of flat yarn we would like to make: the first concerns aspects not brought out in the paper, the others quantitative differences.

Firstly, using Cibalan Blue BRL at 60°C and dyeing samples in separate baths at a liquor ratio of 33 : 1, we found that dye uptake of fabric scoured at 100°C is higher than that of fabric scoured at 60°C. Further, steam setting at low temperatures, e.g. 110°C, considerably reduced dye uptake relative to that of fabric scoured at 60°C and even more so relative to that of fabric scoured at 100°C. In general, at steam-setting temperatures below 120°C, dye uptake did not exceed that of fabric scoured at 60°C. Typical relative values obtained were

	Scouring temperature (°C)		Steaming temperature (°C)			
	60	100	110	115	125	135
Dye uptake	100	118	76	88	111	143

Similar effects were also shown with other classes of dye— Dispersol Fast Red R300 (C.I. Disperse Red 19) and Durazol Blue 2R (C.I. Direct Blue 71).

Secondly, referring to Fig. 8 of the paper, our results with Cibalan Blue BRL show a smaller increase in dye uptake with steaming temperature.

Thirdly, the results in Table VII, comparing the dye uptake of untreated nylon with that of nylon steamed at 25 lb/in² and conclusion 1 under steaming conditions, indicate a threefold increase in dyeing rate on steam setting at 25 lb/in². This does not accord with Fig. 1(*b*) where the increase is much less, or with HATRA work using Cibalan Blue BRL, where steam-set fabric had approx. 40% greater dye uptake than unsteamed fabric.

Mr. PETERS: The dyeing conditions used for Fig. 1 were aimed at obtaining equilibrium and were different from the dyeing conditions used in experiments to compare dyeing rates. Even with these differences, if the dyeing rate is considered at t=30 min, the ratio of the rate of dyeing of the standard yarn to that of the control yarn is 2 : 1.

Mr. JAECKEL: The authors (on p. 609) comment on percentage changes in dyeing rate with heat-setting treatments, and quote approximately 1% differences in dyeing rate for 1 deg. C differences in dry-heat setting temperature. We are happy to agree: with Cibalan Blue BRL dyeings at HATRA for 1 h at 60°C, for 70d/34f/¾ Z nylon 6.6 yarn false-twisted at 80 t.p.i. with 3% overfeed, dye uptake changes per deg. C over the range 198–250°C were, as percentages of dye uptakes at 198, 224, and 250°C, respectively, 1·2, 0·9, and 0·7 (on an absolute basis, 0·105 mg dye/g nylon/deg. C).

For 1 deg. C differences in steaming temperatures, the authors find a 5% change in dyeing rate. Under HATRA conditions we only find half that rate of change: the average increase, as a percentage of dye uptake at 130·4°C, found for separate 1 h, 60°C dyeings of 2% Cibalan Blue BRL at a liquor ratio of 33 : 1 on 205d/34f/1Z yarn of merge number 913G was 2·5%.

Dr. L. ZAKARIAS: A very clear account was presented of the experimentally determined effects of heat setting on the dyeing behaviour on nylon. I am, however, worried about the theoretical explanations and practical conclusions drawn. We have experienced similar problems in heat pretreatments in development work on non-woven fabrics. According to *BP* 776,967 and *BP* 825,002, this non-woven fabric consists of a plurality of thin layers arranged in a certain order of permeability.

The general permeability and dye retention of the fabric are determined and controlled by filtration methods in which the heat-setting of non-woven fabrics (also with nylon layers) is only a small part of our experiments for arriving at practical aerating and dyeing conclusions. Thus the present interesting results obtained by the lecturers could be differently explained and, for practical purposes, radically altered if in the first instance colloid and, especially, collective chemical laws and processes were considered and applied in addition to traditional physico-chemical considerations and macromolecular structures.

Dr. WHITE: We have no comment to make on this question, but note with interest Dr. Zakarias's alternative theory.

Dr. D. PATTERSON: Many of the setting treatments that are described in this paper will alter the physical as well as the dyeing properties of the yarn. Have any attempts been made in the course of this work to obtain relations between both these two types of property and the structural changes in the fibre?

Dr. WHITE: The effect of heat-setting conditions on the mechanical and optical properties of nylon yarns has been studied by the Physics Research Group in the BNS Research Department. The physical and physio-chemical properties of the yarn depend on the fine structure of the polymer and these topics are constantly under investigation by fibre producers.

Mr. H. R. HADFIELD: Would the authors care to explain how they arrived at their summarised results as detailed in Fig. 9?

It is, perhaps, possible for the practical dyer to misinterpret the information presented in Fig. 9. The ability of a dye to cover differences in dyeing properties in nylon is a combination of dyeing rate, equilibrium dye exhaustion and, because of these two properties, migration rate. Fig. 9, at a glance, would indicate that disperse dyes are little better than acid or premetallised dyes and this, of course, from a purely practical viewpoint does not correspond with practice. Could the authors confirm that other factors must also be carefully considered in assessing a dye from a practical viewpoint?

Dr. WHITE: Fig. 9 was derived from our own data published in this paper (acid and metal-complex dyes) and published data on disperse dyes [5, 15]. Fig. 9 shows the general effect of temperature and heat treatment on the rate of dyeing for each class of dye, but it does not compare their actual rates and does not bring out the fact that disperse dyes migrate faster within the fibre and are therefore better for covering certain physical variations in yarns. It is in accord with the observation that dry-heat setting does not alter the general pattern of stripiness but that steam setting can accelerate diffusion of dye into the fibre and give some improvement in levelling. We agree that from a practical viewpoint many points have to be considered in assessing the suitability of dyes for a specific purpose.

Dr. J. K. SKELLY: The somewhat different behaviour of 1:2 metal-complex dyes on dry-heat-set nylon as reported by HATRA [16] and in the present paper is of interest. It is suggested that the two sets of results are not strictly comparable. The HATRA workers used dyeing temperatures of 60°C, while in the present work dyeing was carried out at the boil. It is possible that the state of aggregation of this type of dye at 60°C could be different from that at 100°C, which may partly explain the differences in uptake of dyes reported.

Mr. JAECKEL: With reference to Dr. Skelly's comment, when we referred to physical optical effects causing visual differences in fabrics containing similar amounts of dye, we did not necessarily have different states of aggregation of the dye molecules in mind. We feel that the most important factor is the physical appearance of yarn and of fabric knitted from it. Different false-twisting temperatures produce yarns which feel and look different, and this difference causes the resultant fabrics to look different; this effect of fabric and yarn surface structure tends to persist, even after steaming and dyeing to the same percentage depth. At HATRA we obtained 97·5% exhaustion when separately dyeing samples differently false-twisted, some unsteamed, some similarly steamed, with Cibalan Blue BRL near the boil instead of at 60°C; nevertheless, grey-scale contrast differences were considerable. Internal evidence in the paper suggests to us that the authors' dyeing temperature, not explicitly stated, was probably 85°C.

Dr. WHITE: We agree that the physical appearance of yarn and fibre is important in determining the apparent colour, but this we think is of less interest than the more theoretical aspects. The dyeing temperature was in fact 85°C.

Dr. SKELLY: What is the effect, if any, of the presence of inorganic pigments, e.g. titanium dioxide, or organic pigments in the fibre upon the oxidative process taking place during the dry-heat setting process?

Dr. WHITE: Pigments incorporated into nylon can affect the oxidation of polymer either by direct chemical or catalytic effect or by affecting the crystallisation and fine structure of the polymer, making it more or less permeable to oxygen. Titanium dioxide has little or no effect in the case of the oxidative process in dry-heat setting.

Some organic pigments have a deleterious effect and would be rejected for commercial application, but others containing oxidation inhibitors, e.g. copper, have a beneficial effect.

Mr. A. J. HALL: There is an apparent parallelism between the steam setting of nylon and the treatment of acetate fibres in boiling water, since in both cases the fibre structure is loosened and the dyeing properties are thereby modified. Could this parallelism be extended to include a modification of fibre lustre and the protective effect of tensioning the fibres during the steam treatment?

Mr. PETERS: We have no information on this point.

Mr. C. HOBDAY*: Mr. Peters has emphasised the importance of controlled setting conditions to ensure that maximum coverage of irregularities can be achieved. In bulk processing, however, the

required degree of control is not always achieved. Could the lecturers indicate whether present application techniques, e.g. solvent-assisted dyeing, help in this direction?

Mr. PETERS*: Solvent-assisted dyeing techniques would be of value in covering the type of irregularities referred to.

Mr. W. PENN*: The obvious advantages of setting nylon fabrics in saturated steam prompt the question: has any progress been made with the development of a continuous pressure-steam setting device embodying tension and dimensional control?

Dr. WHITE*: We know that work is being carried out on such a device but have no information on its progress.

Mr. BAMPTON*: The effect of tension during steaming upon the dyeing properties of nylon yarn or fabric may be very marked. Yarn or fabric held under tension to such an extent that shrinkage is restricted will dye to a lighter colour than material which is free to shrink during the steaming operation.

For example, barriness in dyed fabrics sometimes results from a fault in the yarn twist-setting process where the yarn is in some cases wound on to paper tubes. Occasionally part of the tube does not collapse during steaming, so that the yarn at this position shrinks to a smaller degree than elsewhere (Smith, G., *Hosiery Res. Bull.*, **4** (1) 32 (July 1957)).

If the material has not been steamed again at a temperature equal to or higher than that of the treatment causing such a fault, diagnosis may in many cases be facilitated by use of the residual shrinkage technique for the determination of Equivalent Steam Setting Temperature (ESST) (Munden, D. L., and Slater, D., *J. Textile Inst.*, **50**, T393 (1959)). Yarns which have been restricted in shrinkage give a lower ESST.

Dr. WHITE*: It is well known that variations in tension applied during steaming or dry heating can affect the dyeing rate.

Mr. JAECKEL*: We agree wholeheartedly with the authors' comments (bottom of p. 609) on the need to ensure that all commercial heat treatments of nylon yarns and fabrics are controlled and kept as uniform as possible.

In batch processes, such as preboarding of nylon hose and half-hose, the steaming conditions are relatively static. We have repeatedly found that air pockets can sometimes be trapped, particularly with half-hose, causing large reductions in dye uptake; less gross inhomogeneities in steaming conditions, not only between different batches but also within any one batch, i.e. from position to position in the autoclave, sometimes occur and can cause colour variations in hose. Both dyers and machinery makers are aware of this problem, and many attempts at improving the processes have been and are being made by machinery makers.

It is interesting to note that, despite very wide-ranging enquiries, it has not been possible to find a really satisfactory, accurate method of determining the dryness fraction of steam within an autoclave, nor does much attention appear to have been paid to the possibility of using continuous steam flow conditions in boarding processes. Have the authors any views on these matters?

Mr. PETERS*: We have no revolutionary method of determining dryness fraction of steam within a normal supply. We agree that the use of continuous steam flow would be of practical value.

* Communicated

Chairman—Mr. F. M. STEVENSON

Dyeing Polyacrylonitrile Fibres with Cationic Dyes

A Survey and Evaluation of Published Work

W. BECKMANN

Methods for predicting the dyeing behaviour of cationic dyes on acrylic fibres (of Orlon 42 and Dralon types) are of value, since the existence of saturation values, the poor levelling characteristics of the dyes used, and the pronounced dependence of exhaustion rate on dye concentration and temperature demand careful control of the whole dyeing process. The nature of the bond between the fibre and the dye, and the dependence of dyeing equilibrium on dyeing conditions are considered, and equations are derived for calculating the dye uptake of single dyes and of mixtures. Finally, methods of achieving levelness of dyeings are discussed.

Introduction

Considerable difficulties are experienced if an attempt is made to describe the laws governing the elementary operations occurring in the dyeing of textile materials by figures and formulae. The reasons for this are simple: as a rule, complicated, heterogeneous systems and accordingly intricate processes are involved. In consequence, all the important practical knowledge of the past decades, which has led, e.g., to serviceable dyeing recipes, has been gathered almost exclusively by empirical means.

Only in more recent times has the position changed; the careful scientific work on the reactive dyes (particularly in England), to which this class of dye owes its quick advance, is an excellent example. Nevertheless, the processes taking place in dyeing cannot as yet be described quantitatively by means of simple equations between the relevant variables, e.g. temperature, time, concentration, and suitable material constants.

However, this ideal situation can be approached fairly closely in the dyeing of polyacrylonitrile fibres with cationic dyes. In this case two favourable circumstances coincide: firstly, the fibre is fully synthetic, i.e. it is possible to obtain a material with very regular properties, and secondly, the dyeing mechanism is relatively simple. Because of this it is not surprising that several attempts have been made to interpret this dyeing operation theoretically and to describe it numerically. The object of this paper is to provide a survey of these attempts and of the importance of their results to dyeing under practical conditions. In this connection a distinction will be drawn between works dealing with *what* actually occurs during dyeing and those in which attempts are made to describe or formulate the operations *quantitatively* in a more or less practical manner.

This paper is intended to deal only with acrylic fibres of the Orlon 42 and Dralon types, but not with the basified fibres, e.g. Acrilan. Where the word "dye" is used, a cationic dye (i.e. one which dissociates in water into a coloured cation and a colourless anion) is to be understood.

Basic Operations in Dyeing

The important questions that arise when the dyeing mechanism is being considered can be divided into two classes (questions of a purely colouristic nature are not considered here)—

(1) What is the nature of the bond between fibre and dye? Where does the bond occur and what forces take part in bonding?

(2) How does the dyeing equilibrium depend on dyeing conditions? How quickly is equilibrium attained?

These matters will now be considered in detail.

THE NATURE OF THE BOND

In the earliest publications on the dyeing of acrylic fibres, the dyeing properties with cationic dyes are mentioned [1, 2], but, because of the poor light fastness of the dyeings examined, a closer investigation did not appear to be worthwhile. Later, when dyes of considerable fastness to light became available, the assumption was first made that the basic dye was bound, as in a salt, to acid groups [3–5]. No precise particulars were available with regard to the nature of the acid component in the fibre, which was assumed to be either an acid copolymerisate or an acidic hydrogen atom adjacent to the nitrile group [5, 6]. Glenz and Beckmann [7] were the first to report systematic investigations of the nature of the bond. They found that, when equilibrium was established at 80–100°C, Dralon had absorbed approximately the same amount (37 mmoles/kg of fibre) of all the ten cationic dyes examined.

From this fact and from the shape of the measured equilibrium isotherms of dye absorption, they concluded that the cationic dyes were bound to acidic groups, a definite number of which were available in the fibre, probably at the ends of the chains. Glenz and Beckmann were able to determine these acidic groups by means of special titration methods and established that the number of them agreed approximately with the number of chain ends, calculated from the molecular weight. According to Schiffner [8], these acidic groups arise from the anionic polymerisation catalyst—basic dyes have no affinity for basically polymerised

acrylonitrile. Nowadays, however, it is possible for acidic groups to be introduced by other means in order to improve the dyeing properties [9]. Some time later, Vogel *et al.*[10] elucidated the dyeing mechanism for Orlon 42, and found that the sulphur content (0·09%) corresponded to the number of acidic groups present (32 mmoles/kg). Recently, Weltzien and Fester [11] have improved the method of determining the acid groups in acrylic fibres. They also reached the conclusion that Orlon and Dralon carry SO_3H groups at the chain ends which are capable of forming a bond with cationic dyes.

It can therefore be regarded as proved that cationic dyes are bound to acrylic fibres at acidic sites which are present in certain measurable quantities.

In addition, the dye must have some degree of solubility in the fibre, although the proportion of dye thus absorbed is usually low, as can be seen from the slight rise in the equilibrium isotherms above the saturation point [7, 10]. According to Glenz, the dye bound to the acid groups possesses better fastness properties than that which is dissolved in the fibre [7].

Wegmann [12] has put forward an interesting theory. He found that, within an homologous series of cationic dyes, the resistance to exposure to light decreases with increasing basicity of the dye; and from this he concluded that the relatively good fastness to light of many cationic dyes is due to the mutual interaction of the dye and the acrylic fibre. The more homopolar the character of the bond, the greater is the possibility for removal of the energy and consequently the greater the fastness to light.

DYEING EQUILIBRIUM

Very little has been published about the exact position of the dyeing equilibrium. The dyes examined by Glenz and Beckmann [7] were bound practically completely, provided the number of acid groups in the fibre was greater than the number of dye molecules. The affinity (in the thermodynamic sense) of the dyes for the fibre was high. It is known from practical experience that most of the normal commercial dyes behave in a similar manner. Vogel *et al.*[10] also examined dyes whose affinity for the fibre was relatively low. Only equilibrium isotherms for 100°C are given in their paper, no attempt having been made to derive absolute values for the affinity. No further investigations on this particular aspect have been reported; similarly, no quantitative information is available with regard to the effect of temperature on the equilibrium. This is probably due less to experimental difficulties, which are practically non-existent, than to the fact that the affinity of most dyes for the fibre is high. This means that the quantities of dye left in the residual liquor at dyeing equilibrium are so small that the differences between the various dyes are of little practical importance. Only a *very much* lower affinity is of practical significance, in particular as regards levelling and stripping. We shall be reverting to this matter later.

RATE OF DYEING

It is clear therefore that dyeing equilibria have been investigated only to the extent that appeared necessary for practical purposes. The position with regard to the rate of dyeing is similar. In order to understand fully the course of a dyeing process, the individual steps, viz., (*a*) absorption at the surface of the fibre and (*b*) diffusion into the fibre, should be considered separately. The equilibrium position of the first step and the rate of the second jointly determine the actual rate of dyeing.

Absorption is certainly connected with the electrokinetic zeta (ζ) potential of the acrylic fibre, which is highly negative, as for other hydrophobic fibres. Vickerstaff and Weston [13] obtained a value of −44 mV in water. This would seem to show that cationic dyes are attracted and absorbed by the surface of the fibre by reason of their charge. Accordingly, Glenz and Beckmann [7, 14] found that even at very low concentrations of dye in the liquor (approx. 20 mg/l. pure dye) the fibre loses its negative potential and becomes slightly positive as a result of the absorption of dye cations. A further increase of the dye concentration in the liquor alters the potential only very slightly, indicating that the quantity of absorbed dye remains almost constant. Apart from the electrostatic attraction exercised by the zeta-potential, other intermolecular forces can also play a part, e.g. London dispersion forces or dipole forces, so that from the theoretical point of view it is not possible to obtain a clear picture of adsorption as a whole. Unfortunately, there is a lack of experimental data on adsorption isotherms from which quantitative information on the effect of the various factors could be obtained.

No detailed investigations have been made of the second process determining the rate of dyeing, viz. diffusion of dye into the fibre. The reasons why it is more difficult to determine the diffusion coefficients than, e.g., with polyester fibres are—

(1) Mathematical treatment has to take into account that only the dye molecules dissolved in the fibre diffuse freely, whereas those bound to acidic groups do not. As long as free acidic groups are present, molecules continually disappear, by being bound, from the number of diffusing ones.

(2) Most acrylic fibres have an irregular cross-section. The method of Hill [15] for calculating diffusion coefficients from measurements of the absorbed quantity of dye as a function of time cannot be used.

(3) Approximate methods for very short dyeing times (where plane geometry is still applicable) are not suitable because of the influence of adsorption; although the adsorption equilibrium is attained rapidly it cannot be measured quickly enough, so that it is difficult to determine exact data for the beginning of the diffusion process.

Admittedly these difficulties are not insuperable but, nevertheless, they have so far prevented satisfactory treatment of the subject. Instead the overall rate of dyeing has been investigated, i.e. the combined effect of the two processes [7, 16, 17]. This will be considered later, because this type of work usually pursues the practical aim of enabling

predictions to be made about the course of the dyeing process.

Methods of Calculation and Laws of Practical Use

It is clear, therefore, that although the principle of the dyeing mechanism is known, from the theoretical point of view quantitative investigations of many matters would still appear to be desirable. However, proceeding on the basis of dyeing mechanism, some success has been achieved in developing a number of laws which are of practical assistance when dyeing acrylic fibres with cationic dyes. These will now be discussed.

QUANTITIES OF DYE ABSORBED

Since the bonding of the dye cations to the acidic groups in the fibre obeys stoichiometric laws, there is a possibility of calculating the capacity of the fibre for the dye from material constants. Laucius *et al.*[4] first did this for Orlon 42 dyed with Sevron (DuP) dyes and Glenz and Beckmann [7] for Dralon dyed with Astrazon (FBy) dyes; since then Stern [18] has studied further examples. Each dye is allotted a numerical value, which is essentially the number of cationic groups per gram of dye (or its reciprocal) and each fibre another numerical value, the number of acidic groups per gram of fibre. If the number of cationic groups used for dyeing is smaller than the number of acidic groups in the fibre, then almost complete exhaustion of the bath can be expected at equilibrium.

The advantages of this system are obvious, particularly since it can be used with any dye mixtures and even for many retarders and is not dependent on dyeing conditions. Unfortunately, the numerical values used by the various authors contain different factors of proportionality to the actual number of acidic or cationic groups per gram of fibre or dye. For this reason it is not possible to make a direct comparison of the values given by the different authors, although the relative values are consistent. In Table I relative saturation values for the absorption of cationic dyes are given for several commercial types of acrylic fibres.

TABLE I

Absorption of Cationic Dyes by Acrylic Fibres

Fibre	Relative saturation value*	Manufacturer
Acrilan 16	1·4	Chemstrand, U.S.A.
Acrybel	1·2	Fabelta, Belgium
Courtelle	2·8	Courtaulds, U.K.
Crylor	1·4	Soc. Crylor, France
Dolan	1·5	Süddeutsche Zellwolle, Germany
Dralon	1·4	FBy, Germany
Dralon (New)	2·1	FBy, Germany
Exlan L	1·15	Exlan Ind., Japan
Leacryl 16	1·1	Acsa, Italy
Orlon 42	2·1	Du Pont, U.S.A.
Orlon Sayelle	5	Du Pont, U.S.A.
Redon F	1·4	Phrix-Werke, Germany
Tacryl	3·3	Superfosfat, Sweden
Vonnel	1·3	Shinko, Japan

* The value shown is the maximum dye uptake in % of fibre weight for a pure dye of $M \simeq 400$ and high affinity when dyeing equilibrium has been reached; for other dyes multiply by $M/400E$. (M = molecular weight, E = fraction of pure dye in dye).

Since the nature of the acidic groups and that of the copolymer are not the same for all types, the shape of the equilibrium isotherms also varies; some fibres may absorb considerably more dye than indicated by Table I, although the bath is not then exhausted in such cases. The values shown in the table apply when 95% of the dye used is absorbed by the fibre at a liquor ratio of 100:1.

One essential requirement in connection with these calculations is that the equilibrium position of the reaction between dye cation and the acidic group in the fibre is very much in favour of absorption on the fibre, i.e. the affinity is correspondingly high. This condition usually holds for most dyes. Deviations can occur if, in addition to dye cations, there are other cations of high affinity or cations of low affinity present in large numbers, e.g. as when salt is added. However, salt is normally only used when dyeing pale and medium depths, whereas the methods of calculation under discussion are chiefly of interest for full depths.

RATE OF DYEING

In addition to knowing how much dye is absorbed by the fibre at equilibrium, the practical dyer is also interested in knowing how quickly equilibrium is achieved, because this is very important for level dyeing. Glenz and Beckmann [7] established a very marked relation between dyeing temperature and rate of dyeing in the case of Dralon and Orlon 42. For both fibres, whatever the dye used, an exponential relation between temperature and rate of dyeing was found, and the activation energy of dyeing was approx. 72 kcal/mol in each case. The same value can be calculated for Orlon 42 from the data given by Neary and Thomas [19], and only a slightly lower one from the data of Landerl *et al.*[20]. This energy of activation is very high in comparison with values for other dyeing processes. It corresponds to an increase in the rate of dyeing of approximately 30% at a temperature increase of only 1 deg. C. Admittedly this value could depend on particular features of the material, e.g. effects of drawing or heat-treatment, but for all types of acrylic fibres the activation energies and thus the temperature dependence of the rate of dyeing are certainly very high, a fact which is of great importance for practical purposes. The temperature dependence of the dyeing equilibrium in the range 80–120°C can be ignored because it is only slight. It is thus possible to describe the temperature dependence of the entire dyeing process by a simple exponential function—

$$V_T = V_0 \cdot \exp(-E/RT)$$

in which V_T represents the rate of dyeing at the temperature T, R is the gas constant, E the activation energy, and V_0 a constant. The formula is easily used in practice because the activation energy is practically independent of the dye, as indicated above.

Apart from the temperature, the quantity of dye used has an important effect on the rate of dyeing, and it would be useful to have a simple formula to express the relation. Glenz and Beckmann [7] assumed that the rate of dyeing V was proportional to the concentration of dye at the

fibre surface (C_s) and to the number of acidic groups still free in the fibre ($S-C_f$), thus obtaining—

$$V = kC_s(S-C_f)$$

where S = saturation concentration of the dye
C_f = dye concentration in the fibre.

The constant (k) should contain the diffusion coefficient of the dye in the fibre. Taking $C_s \propto C_l$ (C_l = dye concentration in the liquor), the measured results could not be represented by the formula. In such a case, V would have to approach zero as $C_s \to 0$. However, Glenz and Beckmann always obtained a curve in which V tended toward a finite threshold value.

Therefore they assumed that C_s was not proportional to C_l but that— owing to the zeta-potential — it rose rather abruptly at very low values of C_l and only slightly at higher values of C_l. This assumption agrees with conclusions from electrokinetic measurements [7, 14]. An attempt was made to approximate this by putting $C_s = (C_l + z/a)$, where z/a is a measure of the influence of the zeta-potential. The expression for rate of dyeing becomes—

$$V = a(C_l + z/a)(S-C_f) .$$

Although this formula gives fairly good agreement with experimental values, it includes, in addition to the saturation concentration S, two further dye-dependent constants, z and a, and is therefore not suitable for application. However, it does supply some guide to the mechanism of adsorption of the dye at the fibre surface, in agreement with the results of the zeta-potential measurements, and suggests another approach.

According to the figures given by Glenz and Beckmann, there are dyes in which the zeta-potential proportion of the surface charging (z/a) exceeds C_l, even when the dye concentration in the liquor is high. With a dye of this kind the rate of dyeing at the start of dyeing would be almost independent of C_l, or of the quantity of dye used. If one follows a suggestion by Vickerstaff [21] and plots the quantity of dye absorbed in the fibre (C_f) (in mg per g fibre) against the dyeing time (t), the curves obtained at different initial concentrations of dye should have the same initial slope (Fig. 1).

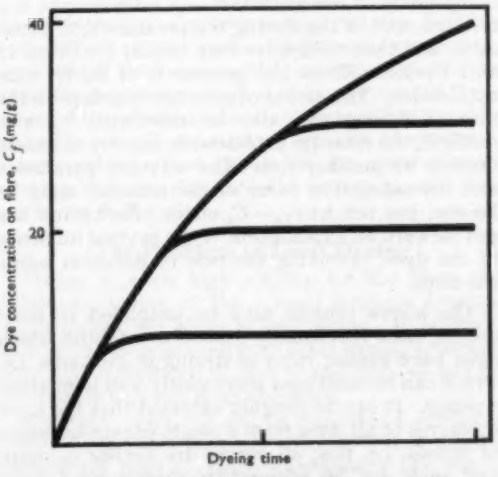


FIG. 1— Rate of uptake of dye (hypothetical curves for different initial concentrations of dye)

TABLE II

Rate of Absorption of Dyes by New Dralon*

Initial dye concn. (%)	Dye on fibre (% of fibre weight) after 3 min	5 min	10 min	30 min
MALACHITE GREEN (C.I. 42000)				
0·2	0·160	0·20	0·20	—
0·4	0·190	0·270	0·40	0·42
0·6	0·195	0·275	0·418	0·495
1·0	0·190	0·270	0·420	0·68
1·4	0·179	0·270	0·420	0·69
ASTRAZON BLUE FGL (C.I. Basic Blue 44)				
1·0	0·80	1·01	1·00	—
2·0	0·77	1·28	1·84	—
4·0	0·89	1·30	2·08	3·60
6·0	0·99	1·36	2·25	3·70

* 2-den, at 100°C and liquor ratio 40 : 1; dye content measured spectrophotometrically.

We examined this type of representation for a number of dyes and frequently obtained a curve similar to that shown in Fig. 1 (Table II). The curves do not level off until more than $\frac{3}{4}$ of the dye present has been absorbed. Theoretically, a levelling off can be expected when the dye concentration at the fibre surface decreases, i.e. when the concentration in the residual liquor drops below 20 mg dye per litre. The height of the asymptotes corresponds to the quantity of dye added, so that the whole series of curves can be easily determined if the enveloping curve, i.e. the curve for the maximum amount of dye used, is known. In other words, such a curve is sufficient to characterise the behaviour of the dye in this connection. On this basis it is possible to obtain convenient material for calculating the absorption of the dye. This has not yet been attempted in practice.

It is interesting to consider whether an expression of the type $C_l \propto t^{\frac{1}{2}}$, which Speakman [22] found to be valid for dyeing processes, is applicable to the enveloping curve; under the existing conditions— dyeing with approximately constant surface concentration— it should apply to the initial dyeing time (diffusion into a level layer). Our experimental results satisfied to some extent an expression of this form. Unfortunately, when dyeing first commences, adsorption, to which other laws apply, is a disturbing factor, so that the straight lines do not pass through the origin and the initial values are inaccurate. At higher concentrations saturation phenomena occur, so that only the middle portion of the curve can be used for determining diffusion coefficients. Individual curves of exhaustion follow the $t^{\frac{1}{2}}$ law much less effectively than the enveloping curve, and this divergence is greater the smaller the quantity of dye used. Fig. 1 shows another reason for the strong dependence of the normal curves of exhaustion (in which the quantity of dye absorbed is represented as a percentage of the amount added) on the quantity of dye added: owing to the surface charging the *absolute* rate of dyeing is at first independent of the quantity of dye added;

then the *relative* rate of dyeing must at first be inversely proportional to the quantity of dye present. A further reason for the dependence mentioned is the saturation of the acidic groups of the fibre surface, so that dye molecules must subsequently diffuse far into the fibre before being bound.

The methods so far discussed for describing the dependence of the rate of dyeing— by means of a formula or by graphs— are not very suitable for practical purposes. Apart from the reasons already mentioned there is another very important point. Mixtures of dyes are normally used in commercial dyeing; this has to be taken into account when formulating systems of calculation which can be used in practice.

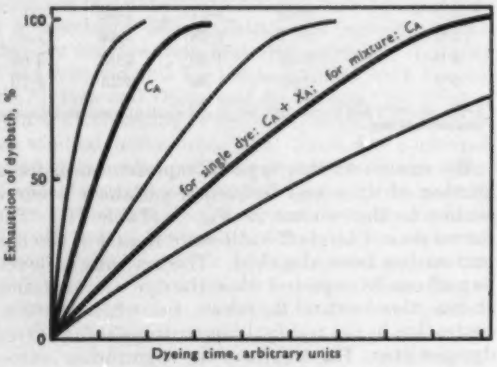


FIG. 2— Exhaustion curves for different initial concentrations of dye A, e.g., C_A, $C_A + X_A$

An attempt to do this has been made by Beckmann [7]. The amount of dye absorbed is plotted, as a percentage of the total amount originally present, against the times of dyeing. As has already been mentioned, these curves are greatly dependent upon the initial quantity of dye present, i.e. the amount of dye added determines the rate of dyeing. It was found that if a dye A of concentration C_A is dyed in the same bath as a dye B of concentration C_B, A will be absorbed by the fibre more slowly than when applied alone at concentration C_A (Fig. 2). The path of the curve of exhaustion for A in the mixture is approximately the same as that of the curve for A alone at a higher concentration, $C_A + X_A$. This concentration $C_{Amix} = C_A + X_A$ is termed the rate-determining concentration of the dye A in the mixture in question, because from it the curve of exhaustion of the dyeing operation results.

The rate-determining concentration of a dye in a mixture is not, as might be assumed, equal to the total concentration of all dyes used, even if the concentration is converted to molar units. It can be calculated, however, according to a simple formula from the quantities of dyes used (C_A, C_B etc.), and from dye-dependent values, so-called mixture parameters p_A, p_B.

$$C_{SAmix} = C_{SA} + \left(\frac{p_A}{p_B} \times C_{SB}\right); \; C_{SA} = \frac{C_A}{S_A}$$

where S_A = saturation concentration of dye A.

The calculated value of the rate-determining concentration $C_A + X_A$ indicates which of a series of curves of exhaustion of dye A is the one applicable to the dyeing in question. This series may be represented by a plot of the time of half-dyeing, or of the time (t_{70}) at which the bath is 70% exhausted, against the quantity of dye added, a so-called t_{70}—C_s curve, whose general form is shown in Fig. 3.

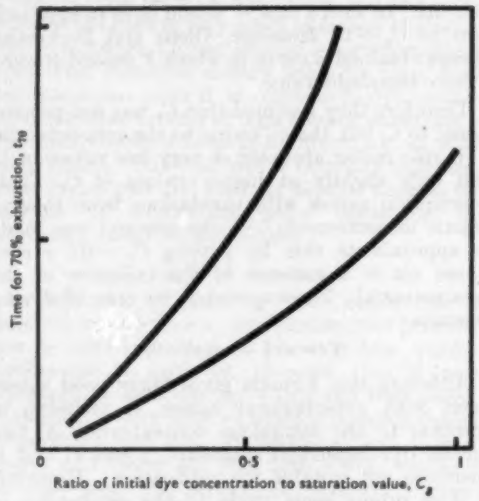
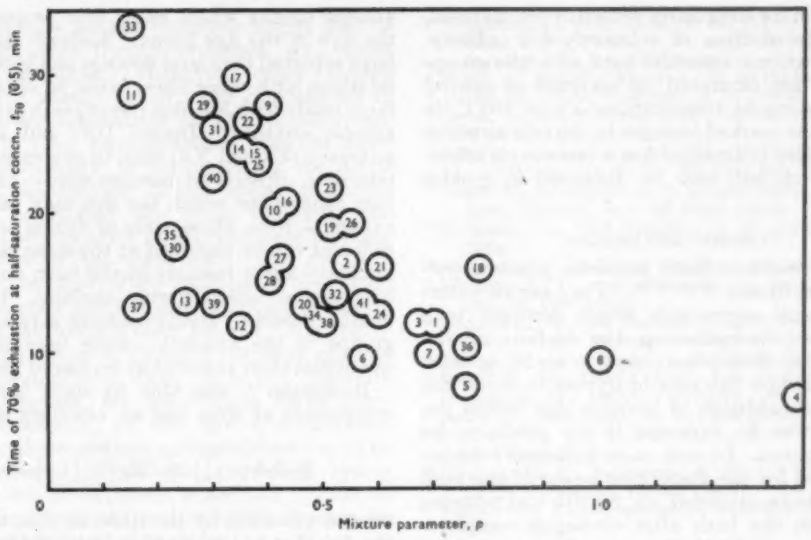


FIG. 3— Typical t_{70}–C_s curves (arbitrary units)

It is therefore possible to calculate for each component of any mixture when 70% of the dye added will have been absorbed. It is necessary to know the mixture parameter of all dyes used and the t_{70}—C_s curve of the dye whose rate-determining concentration is to be calculated. The latter is dependent on the temperature of dyeing and on the liquor ratio. The mixture parameters, which are obtained from measured exhaustion curves of dye mixtures, on the other hand, are independent of concentration and ratio of dyes in a mixture, and of the dyeing temperature and liquor ratio, and their values are very similar for Orlon 42 and Dralon. Thus the process is of fairly wide application. The action of cationic retarders on the rate of dyeing can also be calculated by this method; the retarder is treated in exactly the same manner as another dye. The mixture parameter and the saturation value of the retarder must be known, but not its t_{70}—C_s curve. Beckmann has put forward an explanation of the mutual influence of the dyes, involving the rate of diffusion inside the fibre.

The above process may be simplified to some extent, since it is usually desired to establish which dyes have similar rates of dyeing in mixtures, i.e. which can be combined particularly well in mixture dyeings. It can be roughly assumed that the t_{70}—C_s curves of all dyes form a single-parameter series of curves, i.e. that all curves are similar in shape and each can be adequately characterised by a particular constant. A characteristic value of this



Number	Commercial Name	*Colour Index* No.
1	Astrazon Yellow 8GL	C.I. Basic Yellow 20
2	Astrazon Yellow 7GLL	C.I. Basic Yellow 21
3	Astrazon Yellow 5G	C.I. Basic Yellow 12
4	Yellow	
5	Astrazon Yellow 3G	C.I. Basic Yellow 11
6	Astrazon Yellow GRL	C.I. Basic Yellow 29
7	Astrazon Golden Yellow GL	C.I. Basic Yellow 28
8	Astrazon Golden Yellow GLD	C.I. Basic Orange 29
9	Astrazon Yellow Brown 2GL	C.I. Basic Orange 30
10	Astrazon Orange 2RL	C.I. Basic Orange 28
11	Astrazon Orange 3RL	C.I. Basic Orange 27
12	Astrazon Orange G	C.I. Basic Orange 21
13	Astrazon Orange R	C.I. Basic Orange 22
14	Astrazon Red RL	C.I. Basic Red 25
15	Red	
16	Astrazon Red GTL	C.I. Basic Red 18
17	Astrazon Red BBL	C.I. Basic Red 23
18	Astrazon Red 5BL	C.I. Basic Red 24
19	Astrazon Red 6B	C.I. Basic Violet 7
20	Astrazon Bordeaux BL	C.I. Basic Violet 19
21	Pink	
22	Pink	
23	Astrazon Pink FG	C.I. Basic Red 13
24	Astrazon Blue 3RL	C.I. Basic Blue 47
25	Astrazon Blue RL	C.I. Basic Blue 46
26	Astrazon Blue FGL	C.I. Basic Blue 44
27	Astrazon Blue G	C.I. Basic Blue 1
28	Astrazon Blue 5GL	C.I. Basic Blue 45
29	Astrazon Blue B	C.I. Basic Blue 5
30	Astrazon Red Violet F2R	C.I. Basic Violet 20
31	Astrazon Violet F3RL	C.I. Basic Violet 21
32	Violet	
33	Astrazon Olive Green BL	C.I. Basic Green 6
34	Red	
35	Blue	
36	Astrazon Blue BG	C.I. Basic Blue 3
37	Astra Red 3G	C.I. Basic Red 28
38	Astra New Fuchsine	C.I. Basic Violet 25
39	Astra Violet 3R extra	C.I. Basic Violet 16
40	Astra Diamond Green GX	C.I. Basic Green 1
41	Astra Malachite Green	C.I. Basic Green 4

FIG. 4— Relation of t_{70} (0·5) to mixture parameter, p

kind for the t_{70}—C_s curve is, e.g., the time for 70% exhaustion at the half-saturation concentration, t_{70} (0·5). If the value t_{70} (0·5) is plotted against the mixture parameter, each dye is represented by a point. Dyes whose points lie close together are very suitable for use in mixture in any proportions, whereas dyes whose points lie far apart usually display very varying rates of dyeing in mixtures, as shown in Fig. 4.

The Problem of Level Dyeing

Owing to their high affinity for the fibre, the migrating power of the normal cationic dyes on polyacrylonitrile fibres is only slight. It is therefore more essential than with other dyeing processes that the application of dye to the fibre should be absolutely uniform from the start.

In many cases, control of the rate of dyeing is sufficient for this purpose. At 100°C it is usually sufficiently high to make unnecessary the use of carriers or high-temperature plant, as is customary when dyeing polyester material. Instead the problem often is too high a rate of dyeing. By means of suitable additives and accurate control of the temperature, care is taken to ensure that the dye is absorbed only slowly by the fibre. According to Turner [23], the bath should be exhausted in not less than 45 min. Suitable additives include cationic or anionic retarding agents and neutral salts.

If the material is not uniform, which may be the case for continuous filament, it is often impossible to produce a level dyeing solely by retarding the rate of dyeing, since this cannot prevent the portions of the material which dye more quickly from absorbing more dye at the start than those which dye more slowly. In such cases some degree of migration is essential. Methods of achieving this all aim at preventing complete exhaustion of the bath. Thus, the differences in depth of the various portions of the material do not depend upon the differences in the *rate of dyeing*, but on the *absorption of dye at equilibrium*, which is normally very

uniform, even for irregularly drawn or set material. Use is made of dyes of relatively low affinity, addition of cationic retarders until all acidic groups in the fibre are saturated, or addition of neutral salts and dyeing at temperatures above 100°C, in which case the marked increase in the rate at which the equilibrium is attained has a favourable effect. These methods will now be discussed in greater detail.

CATIONIC RETARDERS

Cationic retarders have acquired great importance in level dyeing [19, 20, 24–27]. They are all water-soluble organic compounds which compete with the dye for absorption on the surface of the fibre and for absorption on the acidic groups. Thus they reduce the rate of dyeing in much the same way as addition of another dye would do. Difficulties can be expected if the goods to be dyed are uneven. In such cases sufficient retarder must be used for the absorption power of the fibre for cations to be exceeded, i.e. for dye and retarder to be left in the bath after dyeing is complete. This results, as already mentioned, in a certain degree of migration or levelling.

The parallelism between the behaviour of dye and that of cationic retarders makes the differences in the action of a retarder with various dyes and the marked dependence of retarder action on concentration understandable. It also enables the quantitative laws previously discussed to be applied to retarders also; degree of retarder action and optimum retarder concentration can therefore be determined.

Cohen and Endler [26] investigated the influence of the chemical structure of retarders on their action. According to them, long-chain (C_{12}) amines produce the most uniform overall rate of dyeing. The anion has no notable effect. An interesting fact was that the retarding action of the quaternary ammonium compounds was generally no better than that of other amino compounds. Cohen and Endler also established that, in the case of amines of chain lengths greater than C_{12}, a time elapsed, which increased according to the length of the chain, before absorption of the dye began. It would appear that such retarders are absorbed very much more quickly than the dye (Sevron Green [C.I. Basic Green 3]).

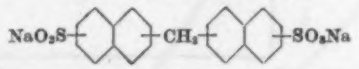
NEUTRAL SALTS

Neutral salts, e.g. sodium sulphate, also retard the rate of dyeing and affect the dyeing equilibrium [20, 24]. It seems that the metal cation also competes for the acidic groups in the fibre. It was also shown that additions of electrolyte reduce the negative surface potential of the fibres [7] and this also reduces the rate of dyeing. Addition of salt thus has a levelling effect, but no quantitative estimation of this effect has yet been attempted. If necessary, the use of about 10% of sodium sulphate is recommended, which permits a reduction of about ⅓ in the quantity of retarder required.

ANIONIC RETARDERS

A further means of preventing the dye from being absorbed by the fibre too quickly is afforded by anionic agents which enter into association with the dye in the dye liquor. Kellet [28] and Leddy [29] have reported that level dyeings on Orlon 42 and its mixtures with other fibres could be obtained much more easily with Maxilon (Gy) dyes in presence of an anionic auxiliary (Irgasol DA) and a non-ionic auxiliary (Tinegal NA) than in presence of cationic retarders. Special advantages were— the temperature range over which the dye may be applied is extended, dyes whose rates of dyeing are normally different can be absorbed at the same rate, and the auxiliary agent remains in the bath and thus still exercises an effect during shading. The anionic auxiliary used by Leddy contains several sulphonic groups in the molecule; when used in sufficient quantities there is therefore no fear of precipitation.

Beckmann [14] was able to show that addition compounds of dyes and an auxiliary of the type



are not absorbed by the fibre, so that temporarily the dye that has reacted is not available for dyeing purposes. This means that, according to the position of equilibrium, the rate of dyeing is reduced to a greater or less extent. The extent of the effect thus depends on the dye used. Another disadvantage is that, in spite of the addition of non-ionic auxiliaries, precipitation of the dye or production of dyeings which are lacking in fastness to rubbing can easily occur. Thus only certain dye combinations are suitable for this process.

DYES OF LOW AFFINITY

It has already been mentioned that to obtain level dyeing it is often not sufficient only to retard the rate of dyeing; migration must also take place. This condition is fulfilled by dyes of low affinity* for the fibre, as reported by Vogel *et al.*[10]. They discovered that these dyes penetrate the fibre more quickly than normal dyes; since, in addition, the bond between these dyes and the acidic groups of the fibre is much weaker, they possess considerable migrating power. They can also be more readily stripped. According to Vogel, retarders are superfluous, but the rate of dyeing can be greatly influenced by addition of salt. The wet-fastness properties at temperatures below 70°C are as good as those of normal dyes, since at low temperatures even a dye of low affinity does not diffuse in the fibre. Disadvantages are, however, experienced in dyeing deeper shades, as the exhaustion of the bath may be low, and in dyeing with mixtures of dye if the dyes are of different affinities.

Conclusion

An attempt has been made to indicate the methods that are available for predicting the dyeing behaviour of cationic dyes on acrylic fibres. The starting-point of these methods is the simple dyeing mechanism. In addition it is always necessary to know certain data for the fibre and dye, which can be regarded as material constants.

* The affinity of cationic dyes can be reduced by means of an electron-donating group (e.g. $-NH_2$, $-OH$), conjugated with the quaternary nitrogen, which weakens the positive charge of the latter [30].

In principle, a similar approach might also be possible for other dyeing processes, e.g. direct dyeing of cellulose. However, other dyeing processes are usually much more complicated in regard to their dependence on measurable quantities and to their reproducibility. On the other hand, there usually is no necessity for those methods of calculation. In the dyeing of acrylic fibres the conditions are quite different; the existence of a saturation value, the poor levelling characteristics of the dyes used, and the pronounced dependence of the exhaustion rate upon dye concentration and temperature demand careful planning of the whole dyeing process. The ability to predict the course of dyeing is therefore of great value to the practical dyer. It is not generally necessary, however, for the dyer to make exact calculations himself, as the dye manufacturers usually take these matters into consideration when offering technical advice and providing dyeing recipes. It was nevertheless considered of interest and value to discuss the problems that have to be overcome before this can be done.

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References

[1] Meunier, P. L., *Amer. Dyestuff Rep.*, **40**, 51 (1951).
[2] Lyle, C. G., Iannarone, J. J., and Thomas, R. J., *ibid.*, **40**, 585 (1951).
[3] Wegmann, J., *Text. Rund.*, **9**, 341 (1954).
[4] Laucius, J. F., Clarke, R. A., and Brooks, J. A., *Amer. Dyestuff Rep.*, **44**, P362 (1955).
[5] Würz, A., *Melliand Textilber.*, **37**, 83 (1956).
[6] Döcke, W., *Dtsch. Textiltech.*, **8**, 77 (1958).
[7] Glenz, O., and Beckmann, W., *Melliand Textilber.*, **38**, 296, 783, 1152 (1957).
[8] Schiffner, discussion in *ibid.*, **38**, 1157 (1957).
[9] e.g. *USP* 2,837,500–1; *BP* 744,487; *Belg. P* 555,500.
[10] Vogel, T., de Bruyne, J. M. A., and Zimmerman, C. L., *Amer. Dyestuff Rep.*, **47**, P581 (1958).
[11] Weltzien, —., and Fester, —., *Dissertation*, Aachen (1960).
[12] Wegmann, J., *Melliand Textilber.*, **39**, 408 (1958).
[13] Vickerstaff, T., and Weston, G., unpublished—see *ibid.*, **35**, 766 (1954).
[14] Beckmann, W., *3rd Internat. Congress on Surface-active Agents*, Köln: Universitätsdruckerei Mainz (1960).
[15] Hill, A. V., *Proc. Roy. Soc., B*, **104**, 39 (1929).
[16] Stern, H., *Ciba Rund.*, **13**, No. 149, 33 (1960).
[17] Beckmann, W., *Melliand Textilber.*, **39**, 1121 (1958).
[18] Stern, H., *Ciba Rund.*, **13**, No. 149 (1960).
[19] Neary, J. P., and Thomas, R. J., *Amer. Dyestuff Rep.*, **46**, P625 (1957).
[20] Landerl, H. P., Iannarone, J. J., and Wilson, J. J., *S.V.F. Fachorgan*, **12**, 668 (1957).
[21] Vickerstaff, T., discussion in *Melliand Textilber.*, **39**, 1126 (1958).
[22] Speakman, J. B., and Smith, L. S. G., *J.S.D.C.*, **52**, 121 (1936).
[23] Turner, G. R., *Amer. Dyestuff Rep.*, **48**, No. 14, 48 (1959).
[24] Clarke, R. A., and Bidgood, L., *ibid.*, **44**, P631 (1955).
[25] Meldrum, K., and Ward, J. S., *J.S.D.C.*, **74**, 140 (1958).
[26] Cohen, S., and Endler, A. S., *Amer. Dyestuff Rep.*, **47**, 325 (1958).
[27] Beckmann, W., *Reyon Zellwolle Chemiefasern*, 452 (1958).
[28] Kellet, H., *Text. Manuf.*, **84**, 313 (1958).
[29] Leddy, J. A., *Amer. Dyestuff Rep.*, **49**, P272 (1960).
[30] American Cyanamid Co., *USP* 2,893,816.

Discussion

Mr. J. KEATON: Can Dr. Beckmann give further details about the calculation of mixture parameters? For instance, is it necessary to obtain the exhaustion curves for all dyes in mixtures with each other, before the requisite mixture parameter can be obtained?

Dr. BECKMANN: The mixture parameter p of a dye is determined as follows:

(1) Exhaustion curves of the dye at three or four different dye concentrations are measured at 100°C. From the results t_{70} (time for 70% exhaustion) (or t_{50}) is plotted against C_s (ratio of actual dye concentration to saturation concentration).

(2) t_{70} of the dye in presence of another dye (with a known mixture parameter) in the bath is measured. From the t_{70}–C_s curve the corresponding value of C_s for the dye in the mixture, $C_{s(mix)}$, is taken.

(3) By means of the equation on p. 620 the value of p of the dye is calculated, all other quantities being known.

Exhaustion curves of the other dyes in the mixture do not need to be measured, but the total amounts and saturation concentrations of every dye present must be known. The measurements are suitably made in a dyeometer.

In Table III, mixture parameters for Orlon 42 and Dralon and the saturation concentrations for Orlon 42 are given for several Astrazon dyes. The values for Orlon 42 and Dralon are very similar.

Dr. A. WÜRZ: While studying the dyeing behaviour of polyacrylonitrile fibres we very often found that the rate of exhaustion in mixture dyeings could not be deduced from the exhaustion curves of the single basic dyes. For this reason we have not published exhaustion curves of Basacryl dyes, since these curves vary a little

TABLE III

Dye*	Mixture Parameter p(Dralon)	p(Orlon)	Saturation concn. on Orlon 42 (% of fibre wt.)
Astrazon Yellow 7GLL	0·50	0·54	7·2
Astrazon Golden Yellow GLD	1·0	0·89	4·3
Astrazon Orange 3RL	0·15	0·19	6·3
Astrazon Red GTL	0·43	0·32	5·4
Astrazon Red BBL	0·34	0·32	5·8
Astrazon Blue 5GL	0·40	0·35	9·0
Astrazon Blue G	0·40	0·41	5·2
Astrazon Olive Green BL	0·15	0·19	7·5

* *Colour Index* Part I numbers are given on p. 621.

although the dyes can be used in mixtures without restriction. Similarly we have not published details of times of half dyeing, since we consider that their value is doubtful for the selection of basic dyes appropriate for dyeing acrylic fibres.

We consider it an advancement that a method has now been developed to determine mathematically the behaviour of basic dyes in mixtures.

It is often stated in the literature that quaternary ammonium compounds block the acrylonitrile fibre if they are used in excess. Dr. Beckmann, also, has mentioned optimum quantities of cationic retarders, the calculation of which presupposes a saturation value and, with it, a blocking concentration.

Our own tests (especially with Basacryl dyes and Germocid) have shown that retarders do not necessarily block the fibre. In these tests we ascertained that the affinity of a dye can be sufficient to displace the retarder, so that we can speak of retardation but not, strictly, of blocking. This effect may, however, depend on the dye used and on the affinity of the quaternary ammonium compounds.

Dr. BECKMANN: In the dyeing of acrylic fibres, cationic retarders behave very similarly to cationic dyes. A saturation concentration for them exists with the same meaning as for cationic dyes, and mixture parameters may be ascribed to them. On this basis optimum retarder quantities—giving dyeing rates presumably best suited for the process—are calculable.

We agree that complete blocking of the fibre, in the sense that *all* acidic sites are rigidly occupied by retarder cations, is not possible in presence of other cations. In equilibrium the number of sites occupied by retarder cations depends on the affinities and concentrations of all the cations present. Cationic retarders, however, always reduce the number of acidic sites available for the dye. This causes part of their efficiency, another part originating from surface effects.

Mr. R. J. HANNAY: Dr. Beckmann's comments on the effect of the addition of cationic auxiliary agents to dyebaths containing cationic dyes in relation to yield and restraining action are of interest. In the paper that I am to present on Friday (see p. 700 *et seq.*), reference is made to the production of resist effects under vat dyes by using a quaternary ammonium compound as resisting agent. Such a procedure works satisfactorily for white resists, but attempts to produce coloured resists using basic dyes resistant to alkaline sulphoxylates as the illuminating colours proved unsuccessful. It was found that printing pastes containing basic dye and a quaternary resist agent gave a lower yield on the acrylic fabric, but where the subsequent vat-dye print fell on the resist print, complete destruction of the basic colour occurred. The lower yield of basic colour can be explained by the competition between the resist and dye for the dye sites in the fibre in the manner outlined by Dr. Beckmann. Can Dr. Beckmann give any explanation for the complete disappearance of the basic colour where the vat-dye overprint falls on?

Dr. BECKMANN: The dyeability of Courtelle with cationic dyes decreases with increasing pH. Moreover, most cationic dyes are not stable in strongly alkaline solutions. Probably the vat-dye overprint contains enough alkali to prevent fixation of the cationic dye.

Dr. R. MCGREGOR: The observation that the absorption of a dye is reduced in the presence of a second dye is common to several dyeing systems: does Dr. Beckmann consider his mixture parameters to be a measure of the interaction of the dyes in solution or in the fibre?

Dr. BECKMANN: According to Valkó, cationic dyes in dyeing liquors are usually not associated. Therefore, we think that interaction of different cationic dyes in solution is only slight in most cases. We have no evidence for direct interaction of the dyes in the fibre, either, but think that dyes influence each other's interaction with the fibre: when two dyes, A and B, with different diffusion coefficients (D) start diffusing into the fibre, the dye (A) with the higher coefficient will find more free anionic sites than B. Therefore B will be more influenced by the presence of A than *vice versa*. This suggests that the mixture parameters are connected with the diffusion coefficients of the dyes in the fibre (the higher D the lower p, other things being equal). Moreover, the mixture parameters will account for direct or indirect interaction of the dyes at the fibre surface.

Dr. MCGREGOR: The statement that the effect of temperature on the dyeing equilibrium in the range 80–120°C is slight presumably refers to dyeings which approximate to exhaustion of the dyebath or saturation of the fibre. It would be very interesting to know the heat of dyeing in this system: has Dr. Beckmann any information?

Dr. BECKMANN: No attempt has been made, as far as I know, to determine the heat of dyeing of cationic dyes on acrylic fibres. It may have quite a high value, although under practical dyeing conditions the exhaustion of the dyebath is usually near 100% in the range 80–120°C.

Dr. MCGREGOR: The graph which the author showed of dye sorbed as a function of $t^{\frac{1}{2}}$ was sigmoidal in shape, the linear portion having an intercept on the $t^{\frac{1}{2}}$ axis. This is characteristic of a system in which the surface concentration of dye increases with time, or in which the diffusion coefficient is a function of x or of t, or in which the surface concentration of dye is not established instantaneously. The curves shown do not support the idea of a constant concentration of dye at the fibre surface during dyeing. Has the author any comments to make on this?

Dr. BECKMANN: With many dyes, for different initial concentrations of dye, the dyeing rate is the same in the initial stages (*see* Table II). This indicates that dyeing takes place from a surface film of dye which is to a large extent independent of dye concentration in the liquor, but not necessarily of dyeing time. The reason why the graphs of dye absorbed vs. $t^{\frac{1}{2}}$ are not linear may be that mentioned by Dr. McGregor.

Mr. D. SIMS: What are the maximum absorptive capacities of some dyes for Orlon 42? Under

what conditions were the rates of dyeing mentioned in the paper measured?

Dr. BECKMANN: The saturation concentrations of some cationic dyes are given in Table III in the reply to Mr. Keaton. Rates of dyeing have been measured in a dyeometer at 100°C and usually at a liquor ratio 40 : 1 at a pH of approx. 4·5.

Dr. McGREGOR*: When the kinetics of dyeing are considered it is usually extremely difficult to differentiate between the kinetics of the diffusion of dye and the kinetics of the associated adsorption processes. What evidence has the author for the statement that the kinetics of the adsorption processes render approximate methods for short dyeing times (p. 617) unsuitable as a means of determining diffusion coefficients? What experimental conditions were used when this aspect was investigated?

Dr. BECKMANN*: We determined the uptake of different cationic dyes by prescoured 3-den. Dralon yarn at 50°C in a dyeometer. Measurable uptake was complete in a few minutes. It was assumed that no diffusion within the fibre took place and all the dye absorbed was on the fibre surface. Depending mainly on concentration and type of dye, we found quantities of 0·05–0·5 mg of dye adsorbed per gram of fibre.

This indicates that for short dyeing times the amounts of dye adsorbed at the fibre surface may not be negligible as compared with the quantity of dye diffused. As it is difficult to differentiate between dye adsorbed and dye diffused, the method in question seems to be unsuitable unless careful studies of the adsorption are also carried out.

Mr. H. R. HADFIELD*: We have had some unfortunate experiences with cationic retarders when applying basic dyes to acrylic fibres. There is a danger, depending upon the relative affinity of the dye and the agent, that the agent may be practically exclusively absorbed first, and subsequently the dye. In this behaviour, although the overall dyeing rate is reduced, in practice there is little advantage, because when the agent is absorbed the absorption of dye is very rapid and practically equal to the absorption of dye in the absence of agent. We agree that this behaviour can be avoided by using a cationic retarding agent with a proper balance of affinity compared with the dye, but as the behaviour of the dyes available varies very widely with any one agent, such a compromise is not generally very satisfactory. Dr. Beckmann has hinted that he has met this state of affairs when he states "in such cases sufficient retarder must be used for the absorption power of the fibre for cations to be exceeded, i.e. for dye and retarder to be left in the bath after dyeing is complete". For this reason it is our view that an unmodified cationic retarder is not a dependable dyeing assistant for basic dyes. Would Dr. Beckmann care to comment?

Dr. BECKMANN*: Cohen and Endler[26] established that the effect mentioned by Mr. Hadfield is dependent on the chain length of the retarder, C_{12} giving the most uniform overall rate of dyeing. In agreement with Mr. Hadfield's experience, we found that the effect is greater the lower the affinity of the dye for the fibre. The passage cited by Mr. Hadfield does not refer to this state of affairs but to dyeing of uneven fibrous material, where, whatever the conditions, different parts of the material dye at different rates.

We agree that cationic retarders of the types now available are not suitable for all cationic dyes. Most of them are designed for dyes with high or medium affinities. Dyes of low affinity are, if necessary, retarded by addition of salt.

* Communicated

The Interaction Forces between Polyacrylonitrile Fibres and Disperse and Cationic Dyes

F. FEICHTMAYR and A. WÜRZ

Results obtained in the field of theoretical chemistry are utilised to investigate the structure of the nitrile group. Recent developments in high-polymer physics are used as a basis to explain the relation between the structure of the polyacrylonitrile fibre and its physical behaviour. The interactions between the nitrile groups of the fibres and disperse dyes, and also between the nitrile groups and cationic dyes, are discussed. Consideration is also given to the interaction between cationic dyes and the anionic groups incorporated in commercial polyacrylonitrile fibres under the conditions of polymerisation. Dyeing tests have been carried out on cyanoethylated cotton to confirm the correctness of the concepts developed with regard to the interaction forces between polyacrylonitrile fibre and cationic dyes.

Several special ranges of dyes for polyacrylonitrile fibres are now available, and many of the dyeing problems have been solved. Nevertheless, sufficient difficulties remain to make a study of the behaviour of polyacrylonitrile fibres during dyeing worthwhile. These difficulties cannot be overcome unless their causes are known, and it is therefore essential to study the mechanism of dyeing and the interaction forces responsible for the dyeing process. Such a study may throw further light on the constitution that dyes must have if they are to satisfy all the demands made by the dyer.

Much has already been written on the mechanism of dyeing of polyacrylonitrile. The papers by Glenz and Beckmann [1] and by Vogel, Bruyne, and Zimmermann [2] probably give the most useful information. These authors conclude that the behaviour of polyacrylonitrile fibres of the Dralon and Orlon 42 types, when dyed with cationic dyes, is due to the anionic groups contained in the polymer chains. These investigations are of great significance for the practical dyer. They have helped the dyer to obtain dyeings with good fastness to rubbing on Dralon and Orlon 42 and to avoid mistakes in the application of retarding agents. The determination of the anion equivalent of these fibres has made possible the calculation of the amount of cationic dye that can be fixed in the fibre by heteropolar bonds. The information given in these studies is, however, not sufficient to provide a comprehensive theoretical understanding of the dyeing properties of polyacrylonitrile fibres, because it does not explain why certain cationic dyes are taken up from the aqueous dyebath by these polyacrylonitrile fibres in quantities substantially exceeding the anion equivalent.

In this paper an attempt is made to throw further light on the dyeing behaviour of polyacrylonitrile fibres by utilising results recently obtained in the fields of theoretical chemistry and high-polymer physics on a molecular basis. We shall deal mainly with the interaction forces that are active within the fibre and also between the fibre and the applied dyes.

Interaction Forces within the Polyacrylonitrile Fibre

THE NITRILE GROUP

In order to understand the interaction forces within the polyacrylonitrile fibre, we must first study the properties and structure of the nitrile group, as this group is the essential feature of the polyacrylonitrile fibre.

The nitrile group is known to be very strongly polar. The dipole moment of aliphatic nitriles in the vapour state, e.g., is approx. 4·0 D*. This indicates that the cohesive forces within the polyacrylonitrile fibre are based mainly on a dipole–dipole interaction. Before discussing this problem in detail, it is advisable to study the linkage conditions within the nitrile group on the basis of modern quantum chemistry and to discuss the reason for this high dipole moment.

It is still often assumed that the polarity of the nitrile group is caused by electron displacements within the carbon–nitrogen triple bond. Quantum chemistry, however, provides us with more precise information on the structure of this group [3], and leads us to believe that its polarity must be regarded as the sum of several components, known as partial moments.

A substantial proportion of the polarity of the nitrile group is due to the lone electron pair on the nitrogen atom. Owing to its asymmetric charge distribution, this electron pair contributes an "atomic" dipole to the total moment of this group. It must also be assumed that the bond between the carbon atom of the aliphatic chain and that of the nitrile group also exhibits an asymmetric charge distribution owing to the varying valency state of the two atoms†, and that this asymmetric charge

* D = Debye = 10^{-18} e.s.u.-cm.

† The following "bond moments" for carbon–carbon linkages have been determined by Petro [4]—

C_{sp^3}–C_{sp^2}	μ = 0·60 D	(toluene)
C_{sp^3}–C_{sp}	μ = 1·48 D	(propyne)
C_{sp^2}–C_{sp}	μ = 1·15 D	(phenyl acetylene)

The following "bond moments" for carbon–hydrogen linkages have been determined by various workers (see Petro [4]) from infrared measurements—

H–C_{sp^3}	μ = 0·31 D	(methane)
H–C_{sp^2}	μ = 0·63 D	(ethylene)
H–C_{sp}	μ = 1·05 D	(acetylene)

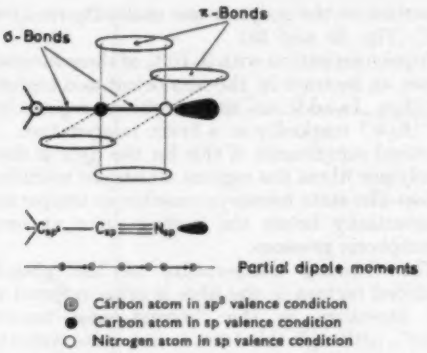


FIG. 1— Electronic structure of the aliphatic nitrile group

distribution contributes a "bond" moment to the total moment of the nitrile group. The third component to be considered is the asymmetric charge of the carbon–nitrogen triple bond.

To illustrate these concepts, Fig. 1 shows the electronic constitution of the nitrile group in a manner which demonstrates the linkage conditions and the various partial moments. The elongated black blob indicates the lone electron pair on the nitrogen atom. This electron pair has a special charge distribution, which is directed away from the nitrile nitrogen. As we shall see later, this lone electron pair is the decisive partial dipole for the interaction between the nitrile groups and cationic dyes.

COHESIVE FORCES WITHIN THE POLYACRYLONITRILE FIBRE

Previous studies of the interaction forces within the polyacrylonitrile fibre were based on the assumption that the polymer chains of this fibre are held together by hydrogen bonds between the tertiary carbon atoms and the nitrile groups [5]. Thus, it was assumed that these secondary valence bonds formed planes in the polyacrylonitrile [6]. Recent experimental and theoretical studies have thrown further light on the nature of the hydrogen bond, and it is now doubtful whether the cohesive forces within the polyacrylonitrile fibre are based on hydrogen bonds [7]. Measurements of nuclear resonance to investigate the inductive effect of the nitrile group [8] do not justify the assumption that the carbon–hydrogen bond of the tertiary carbon atom is so strongly polarised as to permit it to form a hydrogen bond with the nitrile group.

In addition, investigations by Saum [9] into the association of nitriles may now render it necessary to revise past concepts concerning the interaction forces within this fibre, and thus obtain further information on interaction with dyes. By comparing the physical properties, e.g. boiling point, heat of vaporisation, and viscosity, of primary, secondary, and tertiary nitriles, Saum was able to show that the association of nitriles to form dimers must be due to a pronounced dipole–dipole interaction between two nitrile groups. He used the expression "CN-dipole pair bond", as an analogy to the hydrogen bond, and the interaction energy of this CN dipole pair bond is approx. 8 kcal.

PHYSICAL PROPERTIES OF POLYACRYLONITRILE FIBRE

In this section the results of investigations in high-polymer physics will be employed to describe the physical behaviour of polyacrylonitrile fibre. It is known that the dyeing properties of a fibre are heavily dependent on the non-orientated, non-crystalline regions which are accessible to the dye, and also on the conditions governing this accessibility.

X-ray investigations of the fine structure of fibres and infrared spectroscopy normally provide a good indication of the inner structure of fibres. With the aid of these methods it is possible to determine the structure of the crystalline regions and also the relative amounts of crystalline and amorphous regions in many high polymers [10]. Investigations carried out on polyacrylonitrile have shown, however, that the usefulness of these methods is strictly limited for this polymer. Infrared spectroscopic investigation indicates that

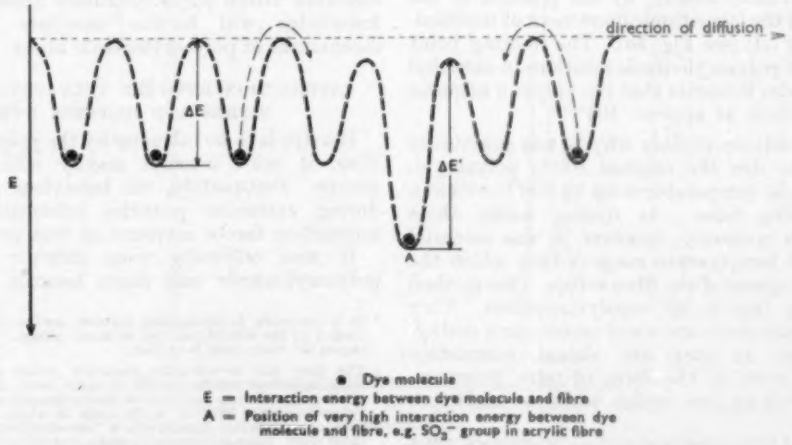

direction of diffusion
ΔE
ΔE'
E
A
Dye molecule
E = Interaction energy between dye molecule and fibre
A = Position of very high interaction energy between dye molecule and fibre, e.g. SO_3^- group in acrylic fibre

FIG. 2— Potential energy curve illustrating the "location change" of dye molecules in the fibre

polyacrylonitrile is neither amorphous nor crystalline; it seems to be mesomorphic. X-ray investigations show that polyacrylonitrile fibres contain mainly regions with a pronounced lateral arrangement of the chain molecules, together with small crystalline regions with a three-dimensional periodic arrangement of chain segments, which appear to have a syndiotactic structure [11]. X-ray investigations do not at present provide an unequivocal answer to the question whether polyacrylonitrile fibres also contain amorphous regions in the conventional sense. As dye is incorporated only in the amorphous regions, it is regrettable that so little information is available about them.

Now, if the dye is to have any possibility of penetrating into the non-orientated regions of the fibre, a process of "location changing" must take place, i.e. it must be possible for an incorporated dye molecule to move out of the "cage" in which it is confined in the fibre and into a neighbouring "cage" which is still free. When this process is demonstrated with the aid of potential energy curves (Fig. 2), it is seen that energy must be fed to the dye molecule to enable it to overcome the barrier between two neighbouring potential energy minima (corresponding to the "cages" mentioned above). This energy is then the activating energy necessary for the "location change" [12].

If processes of this nature are to take place within a finite time (normal dyeing time), the amorphous components of the fibre, which are solidified in a glass-like form, must be at least partly in a condition roughly similar to that of a liquid. In order to achieve this quasi-liquid condition, the fibre must take up sufficient energy to excite certain types of motion* in the polymer. It is only then that energy which can be transmitted by collision is available, thus providing the necessary activation energy for the individual processes taking place in dyeing (including, e.g., diffusion of the dye).

In 100% polyacrylonitrile fibre, the amorphous components enter into this quasi-liquid state within a temperature range around 105°C. This is shown by measurements of the shear modulus (G') or, even more clearly, by the position of the maximum of the logarithmic decrement of mechanical damping (Λ) (see Fig. 3*a*). The freezing point depression of polyacrylonitrile solutions in dimethyl formamide also indicates that the polymer acquires a glass-like form at approx. 104°C [16].

These conditions explain why it was practically impossible to dye the original 100% polyacrylonitrile fibres at temperatures up to 100°C within a normal dyeing time. As dyeing under these conditions is necessary, however, it was essential to lower the temperature range within which the amorphous regions of the fibre soften. One method of achieving this is by copolymerisation. Very suitable comonomers are vinyl acetate and methyl methacrylate, as they are almost completely amorphous, even in the form of pure polymers. Their softening regions, within which certain types of motion in the polymer are excited*, are around 50°C (Fig. 3*b* and 3*c*).

Copolymerisation with 5–10% of these monomers causes an increase in the non-orientated regions of the fibre. In addition, the amorphous regions begin to "thaw" markedly at a lower temperature. The practical significance of this for the dyer is that in copolymer fibres the regions which are solidified in a glass-like state become accessible at temperatures substantially below the boiling point at normal atmospheric pressure.

The freezing temperature of the glass-like, solidified regions in the fibre is often referred to in the literature as the "second-order transition point", although this term is not quite correct†.

Interactions between Fibre and Dye

In dyeing there is an interaction between the dye and the groups of the amorphous regions which are capable of attracting or stabilising the dye. It is therefore impossible to understand the individual processes concerned in dyeing without first discussing the interaction forces responsible for these processes.

Investigations on the position of the distribution equilibria provide some useful information. Glenz and Beckmann [1], and Vogel *et al.* [2], have studied the dyeing equilibria for polyacrylonitrile fibre, and their results indicate that the uptake of cationic dyes by Dralon or Orlon 42 is governed mainly by anionic groups incorporated in the fibre during polymerisation. The number of molecules of dye taken up by the fibre depends on the number of accessible anionic groups, which in turn depends on the dyeing temperature. The dye uptake curve has therefore the form of a Langmuir adsorption isotherm and reaches a saturation value. Any further uptake of dye is governed by the Nernst distribution law, i.e. the dye is dissolved within the fibre.

Whereas only a small amount of some dyes dissolves, large amounts of others dissolve, as can be seen from the dyeing equilibrium graph obtained by Glenz (Fig. 4). It is therefore important to know what relation exists between the constitution of a dye and the extent to which it dissolves within polyacrylonitrile fibres, since such knowledge will further elucidate the dyeing mechanism of polyacrylonitrile fibres.

INTERACTION BETWEEN POLYACRYLONITRILE FIBRES AND DISPERSE DYES

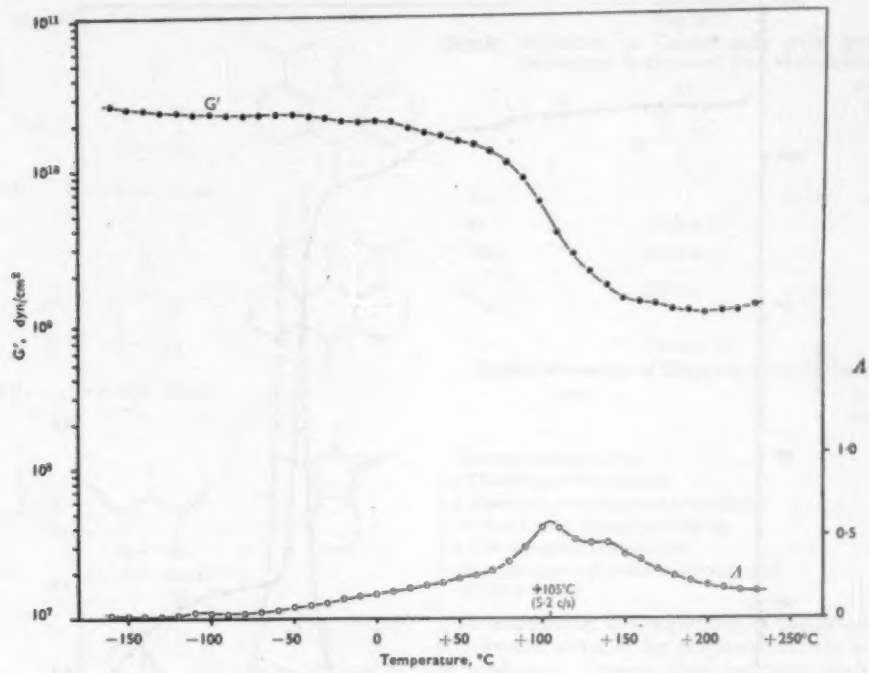
If a dye is to be taken up by the polyacrylonitrile fibre, it must interact mainly with the nitrile groups. Fortunately, the behaviour of this fibre during extrusion provides information on the interaction forces involved in this process.

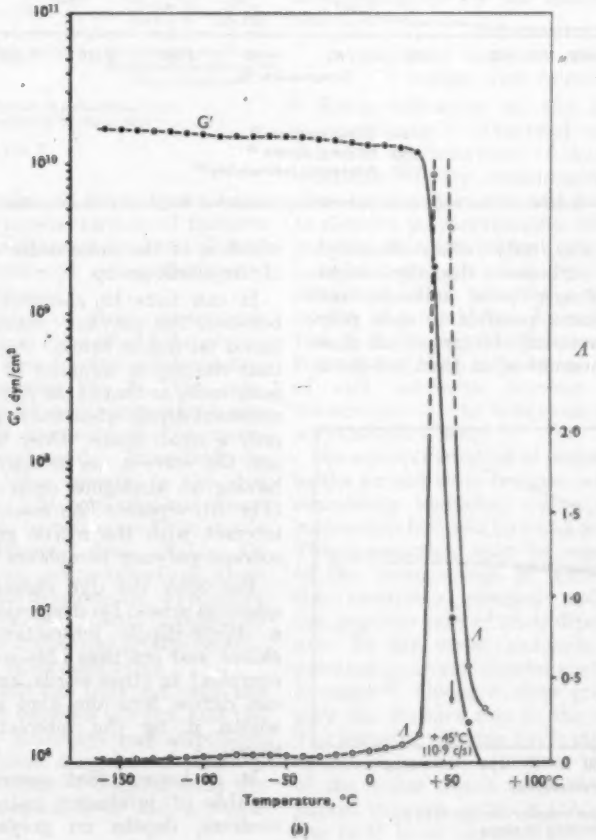
It was originally very difficult to convert polyacrylonitrile into fibres because no solvents

* It is necessary to distinguish between motion of the chain and motion of the side-chains and terminal groups.

* It is necessary to distinguish between motion of the chain and motion of the side-chains and terminal groups. In the softening region the main chain is excited.

† The first- and second-order transition points are actually the temperatures at which changes in state occur, during which the whole system is in a condition of thermodynamic equilibrium. The "glass transition interval" is the range in which a change from a state of equilibrium (liquid) into a "non-equilibrium state" (glass) takes place. Glass also tends to a state of equilibrium, but this is not achieved within a finite time.


G'
Λ
+105°C
(5·2 c/s)
G', dyn/cm²
Temperature, °C
(a)


G'
Λ
+45°C
(10·9 c/s)
G', dyn/cm²
Temperature, °C
(b)

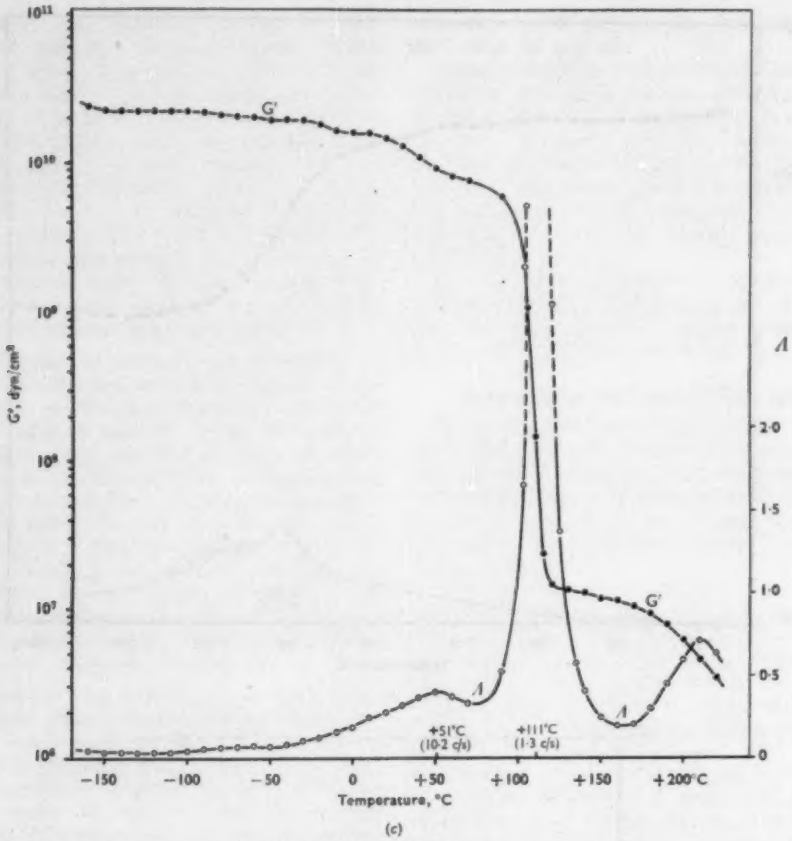


FIG. 3— Shear modulus (G') and logarithmic decrement of mechanical damping (Λ) as a function of temperature

were available. It was only when dimethylformamide, ethylene carbonate, dimethyl sulphoxide, and other strongly polar solvents were employed that it became possible to spin polyacrylonitrile. A characteristic feature of all these solvents is a dipole moment of at least 3·6–3·8 D, which is of the same order as the dipole moment of the nitrile group.

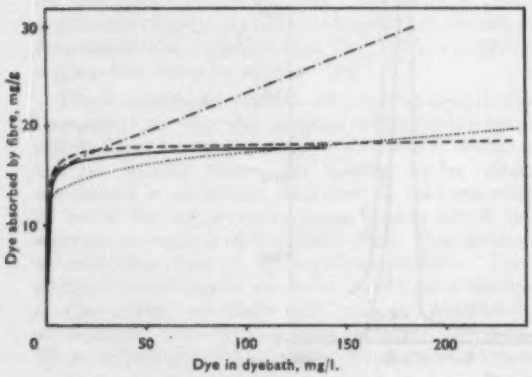


FIG. 4— Equilibrium isotherms of cationic dyes on Dralon, according to Glenz [1]

It can thus be assumed that the interaction between the polymer chains and the solvent is based on dipole forces. An essential condition is that the dipole moment of the solvent is of the same order as that of the nitrile dipole, and that the resultant dipole is located in a group which occupies only a small space. Only under these conditions can the solvent, as comparison with compounds having an analogous open-chain structure shows (Fig. 5), separate the associated polymer chains, interact with the nitrile groups, and thus form solvent–polymer complexes [17].

For both the dye chemist and the dyer the question arises: Do dyes exist which are capable of a dipole–dipole interaction with the polymer chains and are thus able to form a dye–polymer complex? In other words, are there any dyes which can diffuse into the fibre and become stabilised within it by the interaction energy liberated there?

It is known that several disperse dyes are capable of producing pale, and in some cases medium, depths on polyacrylonitrile fibre. A

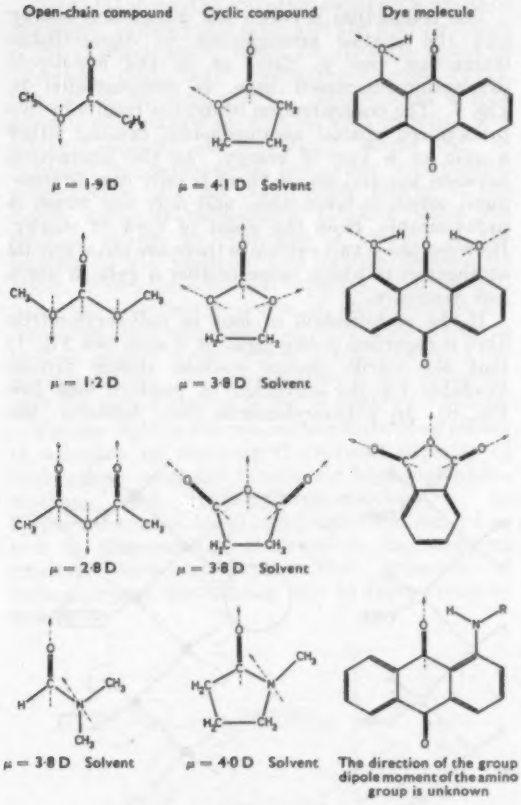

Open-chain compound
Cyclic compound
Dye molecule
μ = 1·9 D
μ = 4·1 D Solvent
μ = 1·2 D
μ = 3·8 D Solvent
μ = 2·8 D
μ = 3·6 D Solvent
μ = 3·8 D Solvent
μ = 4·0 D Solvent
The direction of the group dipole moment of the amino group is unknown
The broken lines indicate the direction of the partial dipole moments of the groups

FIG. 5

study of the constitution of these dyes shows immediately that they possess structural features similar to those of the solvents mentioned above; they all contain a hydroxyl or amino group adjacent to a carbonyl group.

The structural formulae of these compounds show that the partial dipole moments of the groups are additive, as is also true for the corresponding solvents for polyacrylonitrile (Fig. 5). The comparable groups are spatially more distant from one another, but the dipole moments of the corresponding carbonyl compounds, measured in benzene[18], show that these groups in the dye molecule also have a very high total dipole moment (Table I). Measurements in benzene of the dipole moments[19] of the disperse dyes (Table II) commonly used for dyeing polyacrylonitrile fibres do not provide any reliable information. Symmetry conditions in the molecules cause oppositely directed moments of the functional groups responsible for the polarity to offset each other.

It must also be pointed out that not only the dipole–dipole interaction between the dye and the nitrile groups, but also induction and dispersion forces, play a role which may be of decisive importance, as they are closely coupled with the electrostatic forces discussed here and increase their attraction.

TABLE I

Dipole Moments of Compounds with Structures Analogous to those of Dye Molecules

R=		R′=H	R′=CH_3
–H	2·93 D	—	—
$-CH_3$	3·10 D	—	—
	3·38 D	1·92 D	2·01 D

TABLE II

Dipole Moments of Disperse Dyes in Benzene

Dye	Dipole moment D
1-Aminoanthraquinone	1·5
1,4-Diaminoanthraquinone	2·8
1,4-Diamino-2-methoxyanthraquinone	3·1
1-Amino-4-hydroxyanthraquinone	2·9
1,4-Dihydroxyanthraquinone	2·6
1-Methylamino-4-β-hydroxyethylamino-anthraquinone	4·8

In conclusion, a comparison of the constitution of solvents suitable for polyacrylonitrile and that of analogous disperse dyes indicates with a fair degree of certainty that dipole–dipole interactions are responsible for the interaction between dye and fibre.

INTERACTION BETWEEN POLYACRYLONITRILE FIBRES AND CATIONIC DYES

Some indication of the interaction between polyacrylonitrile fibres and cationic dyes can be found in the behaviour of these fibres toward salt solutions. Highly concentrated aqueous solutions containing certain uni- and bi-valent ions are able to dissolve polyacrylonitrile fibres. The important point is that the solvent properties of these salt solutions are governed by the type of anion contained. This provides a valuable clue to the uptake of cationic dyes by polyacrylonitrile fibres. Before discussing this problem in detail, however, it is advisable to consider generally the condition of salt solutions, because this will provide information on the behaviour of dye salts in polyacrylonitrile fibres.

An aqueous solution of sodium chloride is always in the ionised state because cations and anions are completely hydrated, owing to the electrostatic interaction between ions and polar water molecules. This interaction may be regarded as the result of the arrangement of water molecules around the positively charged sodium ion so that the negative part of their dipoles faces the sodium ion. In the water molecule, too, lone electron pairs act as atomic dipoles contributing to the total moment[20]. Owing to their position, they actually play the decisive role in the solvation of cations. The negative chloride ion is stabilised by the water molecules in such a manner that the positive side of the water dipole faces the chloride ion. The partial moment active in this connection is mainly the H–O bond moment (see Fig. 6).

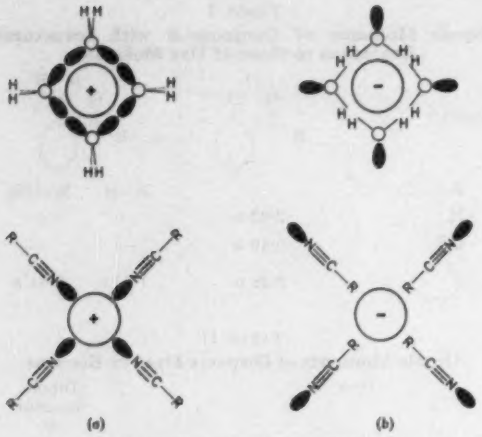


FIG. 6— Solvation of cations and anions by (*a*) water molecules, (*b*) alkyl nitriles

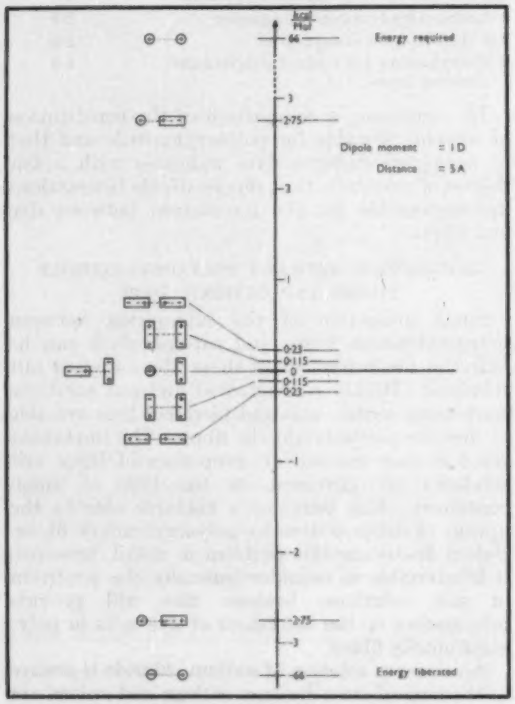


FIG. 7— Ion–ion, ion–dipole, and dipole–dipole interaction energies for a dipole moment of 1 Debye unit and a distance of 5 Å

The connection between the interaction energy and the spatial arrangement in dipole–dipole interaction (see p. 630), or in the ion–dipole interaction discussed here, is demonstrated in Fig. 7. The concentration of dipoles results in two pronounced spatial arrangements, causing either a gain or a loss of energy. In the interaction between ion and dipole there is only one arrangement which is favourable, and only one which is unfavourable, from the point of view of energy. Between these two extremes there are other spatial arrangements which cause neither a gain in nor a loss of energy.

If the stabilisation of ions in polyacrylonitrile fibre is regarded in this light, it is seen (see Fig. 1) that the nitrile groups contain atomic dipoles available for the solvation of positive ions (see Fig. 6). In polyacrylonitrile fibre, however, the

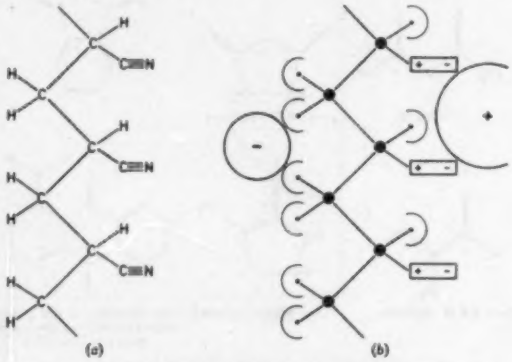
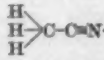
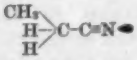


FIG. 8— (*a*) Acrylonitrile chain in isotactic configuration, (*b*) steric arrangement of the nitrile dipoles of polyacrylonitrile fibre, showing potential solvation conditions

positive part of the dipole required for the solvation of the negative ion is blocked sterically to a large extent by the polymer chain (see Fig. 8). Consequently, the energy gained by the stabilisation of a negative ion in the fibre cannot be significant. Little energy is gained for the solvation of dye cations and their corresponding colourless anions, when the process is regarded as a whole.

In order to investigate the validity of these concepts, we have studied the solvation capacity of nitriles for salt-like compounds. The fact that the amorphous regions of polyacrylonitrile fibres are quasi-liquid at high temperatures shows that there is justification for comparing low-molecular-weight nitriles with polyacrylonitrile fibres in this manner.

TABLE III
Solvent Capacity of Nitriles

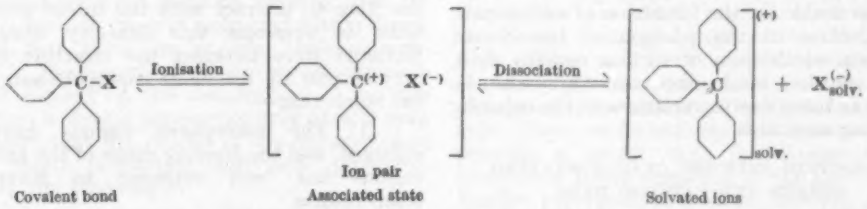
	N≡C–C≡N	H–C≡N		
Solvent capacity for salts	Nil	Good	Good	Good
Dissociation power [11]	—	0·9*	0·5†	0·4†
Solvation capacity				
(*a*) Cations	Good	Good	Good	Good
(*b*) Anions	Nil	Good		

decreases →

* Dissociation constant α of 0·1-M KI
† Dissociation constant α of 0·1-M $[(C_2H_5)_4N]$ I

Table III shows the solvation capacity for salts of cyanogen, hydrocyanic acid, and the first members of the aliphatic nitrile series, for salts. It would be expected that only hydrocyanic acid could, because of its strong $H–C_{sp}$ dipole, form a true solvate with anions as well as with cations. The solvent capacity of stabilising anions can be expected to decrease in the order acetonitrile, propionitrile, etc., as the positive charge of the nitrile dipole is increasingly blocked, while the positive charge in cyanogen is located in the interior of the molecule and cannot develop its effect. When the solvation capacity, and in particular the dissociation power, of these nitriles are compared, it is seen that the structural change is evident mainly in the degree of dissociation of the dissolved salts. This observation is in conformity with the poor solvation power of nitriles for anions.

Further light is thrown on the stabilising effects of solvation by studying the solvent capacity of hydrocyanic acid and nitriles for triphenylchloromethane and triphenylbromomethane[22]. In hydrocyanic acid, these compounds are ionised as well as dissociated, and therefore the solutions conduct electricity well. The processes of ionisation and dissociation can be represented as follows—



This indicates that the energy liberated by the solvation of the two ions is sufficiently large to permit a heterolytic splitting of the homopolar bond between the carbon atom and the chlorine or bromine atom. In contrast to hydrocyanic acid, nitriles produce only a slight dissociation of triphenylchloromethane. In the latter case, the total solvation energy of cation and anion is inadequate to cause a heterolytic splitting of the carbon–halogen bond.

We have also attempted to obtain information on the state of solution of dye salts in nitriles by determining solubility and measuring conductivity. The results of our solubility measurements, which were carried out on Crystal Violet (C.I. Basic Violet 3) salts, are given in Table IV. They show that solubility measurements of this kind provide no specific information about the condition of dissolved dye salts. On the other hand, conductivity measurements indicate clearly that dye salts of this type are associated in nitriles. A similar association can also be expected in the case of cationic dyes containing an external quaternary ammonium group. This may be assumed from the dissociation constants (α) given in Table III for tetraethylammonium iodide.

Observations made in the past on the behaviour of electrolytic solutions in non-aqueous systems

TABLE IV

Solubilities (mol %) of Crystal Violet Salts in Nitriles

Solvent	Crystal Violet			
	Cl	Br	I	ClO_4
Acetonitrile	1·343	2·259	0·804	1·414
Propionitrile	0·280	0·574	0·636	0·817
Butyronitrile	0·280	0·424	0·499	0·499
Benzonitrile	2·195	2·700	0·960	1·756

may be of assistance in arriving at a better understanding of these association processes. It has long been known that cations and anions combine to form an ion pair when the solvent has a low dielectric constant and is not capable of solvating the individual ions. This can be conceived as a process in which the anion is incorporated in the solvate envelope of the cation, if the solvent cannot solvate the anion.

The physical behaviour of ion aggregates of this type differs from that of solvated ions. Thus, if an electric field is applied to a solution of solvated ions, the ions (often with their solvate envelope) move in the direction of the oppositely charged electrode. Ion pairs, on the other hand, interact as polar molecules with the electric field (and also with the solvent) and are orientated in this field. The dipole moments of quaternary ammonium salts in benzene solution[23], e.g., can be measured, as these salts are almost completely dissolved in ion-pair form in this solvent (Table V).

TABLE V

Dipole Moments of Quaternary Ammonium Salts in Benzene Solution

Ammonium Salt	Dipole Moment (D)
$[(n\text{-}C_4H_9)_4N]$ Br	11·9
$[(n\text{-}C_4H_9)_4N]$ ClO_4	14·1
$[(n\text{-}C_4H_9)_4N]$ acetate	11·2
$[(n\text{-}C_4H_9)_4N]$ picrate	13·1
$[(n\text{-}C_4H_9)_2NH]$ I	8·09
$[(n\text{-}C_4H_9)_2NH]$ Br	7·61
$[(n\text{-}C_4H_9)_2NH]$ Cl	7·17

In addition to ion-pair formation, there are other ways of forming the most suitable arrangement, from aspects of energy, in a given solvent. If the structures of solvent and solute are suitable, there is no reason why two cations and two anions should not form an aggregate, which would then have the character of a quadripole. It should also be possible to form still larger aggregates, multipoles.

These conceptions of the state of solution of salts in nitriles also apply to dye salts in polyacrylonitrile fibres. Here, however, the solvate

envelope of the dye cation is not formed completely. This is because the nitrile groups in the polyacrylonitrile fibre are firmly attached to the polymer chains and thus have very low mobility. Only to a small extent are they able to move into the positions most favourable from the aspect of energy. The dissociation equilibrium of the dye salts dissolved in the fibre is, therefore, in favour of association. The process of dyeing polyacrylonitrile fibre which contains no anionic groups with cationic dyes is apparently based mainly on the incorporation of ion pairs. These are stabilised to a varying extent as dipoles by interaction with the dipoles of the fibre.

Some indication of the extent of these ion-pair dipoles can be obtained from Table V, in which the dipole moments of quaternary ammonium compounds are given. These values also apply approximately to ion pairs of cationic dyes with an external basic group. For these dyes ion-pair formation is favoured when at least one of the valencies of the nitrogen is not blocked by a large group. For instance, if there is only an N–H bond, the small space occupied by this bond permits the positive and negative ions to approach one another closely, thus releasing sufficient interaction energy for a very stable ion pair to be formed. If the proton is replaced by a methyl group, the situation is less favourable for the formation of an ion pair. The variations in the position of the Nernst distribution equilibrium of various cationic dyes, i.e. the solution mechanism, can thus also be regarded as being due to variations in the capacity for forming associates.

INTERACTION BETWEEN CYANOETHYLATED COTTON AND CATIONIC DYES

The dyeing properties of a fibre depend not only on the number of groups which attract and combine with dyes, but also on the accessibility of these groups. In pure acrylonitrile polymers, not all the nitrile dipoles capable of solvating dye cations, including those in the amorphous regions of the fibre, are readily accessible. As a control, we have carried out tests on cyanoethylated cotton on the assumption that the nitrile groups of this fibre are readily accessible and can freely develop their attraction for the dye cation.

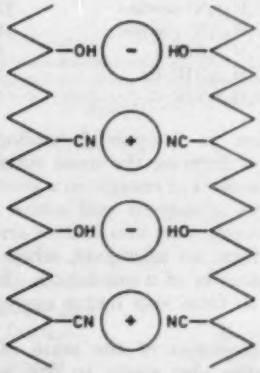


FIG. 9— Cations and anions in cyanoethylated cotton, showing potential solvation conditions

Cotton has a high adsorption capacity for anions. This is without doubt connected with the fact that the solvate envelope of anions in alcohols in general is exceptionally well formed. Cyanoethylation modifies the cotton in such a manner that the fibre can be expected to form good solvates for cations as well as for anions. And, indeed, in dyeing with cyanine dyes, it is found that the depth of dyeing obtained increases as the nitrile group content of the cyanoethylated cotton increases, although the dyes employed cause no significant staining of cotton or of acrylic fibres containing no anionic groups.

Fig. 9 provides an illustration of a possible way in which a cationic dye is stabilised in cyanoethylated cotton. Although several other factors which have not yet been investigated are doubtless concerned in the process, we feel that the results obtained are an indication of the correctness of the concepts developed above.

INTERACTION BETWEEN POLYACRYLONITRILE FIBRES CONTAINING ANIONIC GROUPS AND CATIONIC DYES

The cohesive forces in even the amorphous regions of pure polyacrylonitrile fibre are so high (the glass-transition point is above 100°C) that dye in boiling dyebaths diffuses only very slowly into the fibre to interact with the nitrile groups. In order to overcome this difficulty, fibre manufacturers have loosened the structure of polyacrylonitrile by means of copolymerisation, with the result that—

(1) The amorphous regions have been enlarged, and the freezing range of the amorphous regions has been extended to cover lower temperatures.

(2) Groups with affinity for the dye have sometimes been incorporated.

In the case of polyacrylonitrile fibres containing no anionic groups, we have seen that the incorporation of cationic dyes is possible only when cation and anion are solvated simultaneously or when an ion associate is stabilised. In all cases, the anion associated with the dye cation must be incorporated in order to maintain electrical neutrality. If the fibre contains anion-forming groups resulting from the process of polymerisation, incorporation of the anion associated with the dye cation becomes unnecessary. Obviously, this is a far better method, from aspects of energy, than the simultaneous uptake of dye cations and dye anions.

The nitrile groups of polyacrylonitrile fibre have only low mobility and are unable to solvate cations and anions completely. It can therefore be assumed that the dye cations form ion pairs with the anionic groups of the fibre. In this case, this means that the anion polymerised into the fibre forms part of the solvate envelope of the dye cation*.

In connection with the ion-pair formations discussed here, it is not possible to give any definite information on the connection between chemical constitution and interaction energy. For

* This ion-pair formation is generally referred to in the literature as the mechanism of salt formation. We feel that the term "ion-pair formation" is preferable, as it is more closely related to the terms used in general chemistry.

the purposes of practical dyeing, however, the structure of all dyes belonging to one range should be based on the same principle, in order to ensure minimum variation between the interaction energies for ion-pair formation with the individual dyes. If this is not so, it will be very difficult to select dyes with the same rate of uptake when mixture dyeings are to be made.

The main groups of cationic dyes employed today in dyehouses in Europe for dyeing polyacrylonitrile fibres of the Orlon 42 and Dralon types either contain an external quaternary ammonium group or have a quaternary nitrogen atom incorporated in the chromophoric system. The essential difference between these two groups is that the positive charge in dyes with external quaternary ammonium salts is localised, whereas in dyes of the cyanine type, e.g. Basacryl dyes, it is partly delocalised.

In dyes of these two types, the spatial conditions in respect of the electronic structure of the molecules for the ion-pair formation mentioned above vary. These variations have an influence on the amount of interaction energy liberated, which in turn governs the affinity of the dye. This may help to explain the variations in the fastness to cross-dyeing of dyeings of cationic dyes.

In summarising the methods whereby dyes are bound in various types of polyacrylonitrile fibres, we find that there are specific "linkage components". These components are specific for each dye and depend on the constitution of the dye salt. Thus, in dyeing polyacrylonitrile fibre, it may be assumed that the process of dye incorporation is the result of several individual processes, including the following—

(*a*) ion-pair formation between dye cation and the anionic groups incorporated in the fibre by polymerisation

(*b*) ion-pair formation between dye cation and dye anion

(*c*) solvation of dye cations and the anionic groups incorporated in the fibre by polymerisation (the anion incorporated by polymerisation is not a direct component of the solvate envelope of the dye cation)

(*d*) solvation of dye cation and dye anion.

For processes (*a*) and (*c*) the anionic fibre equivalent is of significance, while processes (*b*) and (*d*) are governed by the mechanism of solution. The total affinity of the dye for the fibre is therefore the sum of a number of affinity factors, each of which is based on specific interaction forces.

For the ion-pair formation between dye cation and anionic group (*a*), the equilibrium is mainly in the direction of dye incorporation in the fibre. The counter-reaction to (*a*), coupled here with ion-pair formation, consists in the donation of a proton (hydroxonium ion) to the liquor, and it is obvious that this total process leads to the liberation of a large amount of energy. The solution process (*b*) and (*d*) consists in the following reactions. Dye cation and the colourless anion, which are hydrated in the liquor, lose this hydrate sheath when they enter the fibre, and solvate in the polyacrylonitrile fibre as ions or as an ion-pair (dipole molecule). The energy balance is obviously far less favourable for this process than for ion-pair formation with the anionic group incorporated by polymerisation. This solution process thus permits in most cases only a very slight uptake of dye by the fibre. Exceptions occur when, for steric reasons, reactions take place between dye cations and dye anions with formation of aggregates which can be exceptionally readily solvated in the fibre.

Electrokinetic Potential of Polyacrylonitrile Fibre

We have hitherto been concerned mainly with interactions occurring in the polyacrylonitrile fibre. In order to understand the processes involved in the dyeing of this fibre, however, we must also discuss the interactions which occur at the fibre–liquor interface.

A factor which may assist us in this respect is the electrokinetic potential (zeta potential) of the fibre. Glenz and Beckmann[1] measured this quantity for Dralon. They found that this fibre acquires a strong negative charge when immersed in water. This charge becomes even greater when salts are added in small quantities, but decreases with increasing salt concentration. When cationic dyes which are suitable for dyeing polyacrylonitrile fibre are added, even in small quantities, this causes a change in sign of the charge on the fibre. Glenz and Beckmann also observed that the zeta potential also influences the rate of absorption of cationic dyes by fibres of the Dralon type. Their results indicate that the zeta potential provides a useful basis for discussion of the interaction forces operating at the fibre interface. Further experimental work is, however, necessary before an attempt can be made to interpret the interfacial processes as molecular phenomena.

* * *

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References

[1] Glenz, O., and Beckmann, W., *Melliand Textilber.*, **38**, 296, 783 (1957); Glenz, O., *ibid.*, **38**, 1152 (1957).
[2] Vogel, T., De Bruyne, I. M. A., and Zimmermann, C. L., *Amer. Dyestuff Rep.*, **47**, 581 (1958).
[3] See Moffitt, W., *Proc. Roy. Soc. A.*, **202**, 534, 548 (1950).
[4] See Petro, A. J., *J. Amer. Chem. Soc.*, **80**, 4230 (1958).
[5] See Schildknecht, C. E., *Vinyl and Related Polymers*, New York: John Wiley (1952).
[6] Ray, L. G., *Text. Research J.*, **22**, 144 (1952).
[7] See Liang, C. Y., and Krimm, S., *J. Polymer Sci.*, **31**, 513 (1958).
[8] See Dailey, B. P., and Shoolery, J. N., *J. Amer. Chem. Soc.*, **77**, 3977 (1955).
[9] Saum, A. M., *J. Polymer Sci.*, **42**, 57 (1960).
[10] See Hendus, H., Schnell, G., Thurn, H., and Wolf, K., *Ergebn. exakt. Naturwiss.*, Bd. 31, 221, Springer-Verlag, Berlin-Göttingen-Heidelberg (1959).
[11] See Stéfani, R., Chevreton, M., Terrier, J., and Eyraud, Ch., *Compt. rend.*, **248**, 2006 (1959); Stéfani, R., Chevreton, M., Garnier, M., and Eyraud, Ch., *ibid.*, **251**, 2174 (1960).

[13] See Glasstone, S., Laidler, K. J., and Eyring, H., *The Theory of Rate Processes*, Chapter IX, New York and London: McGraw-Hill (1941).
[14] Schmieder, K., and Wolf, K., *Kolloid Z.*, **134**, 149 (1953).
[15] Wolf, K., and Schmieder, K., *Simposio Internazionale di Chimica Macromolecolare*, Torino (1954); *Ricerca Sci., Suppl.*, **A25**, 732 (1955).
[16] Schmieder, K., and Wolf, K., *Kolloid Z.*, **127**, 65 (1952).
[17] Krigbaum, W. R., and Tokita, N., *J. Polymer Sci.*, **43**, 467 (1960).
[18] Würstlin, F., private communication.
[19] Feichtmayr, F., and Würstlin, F., unpublished.
[20] Kramer, B., *Reyon Zellwolle Chemiefasern*, 607, 682 (1955).
[21] See Pople, J. A., *Proc. Roy. Soc. A*, **202**, 323 (1950).
[22] Walden, P., *Elektrochemie nichtwässrigen Lösungen*, Leipzig: Barth Verlag (1924); *Molekulargrössen von Elektrolyten in nichtwässrigen Lösungen*, Leipzig: Steinkopf-Verlag (1923).
[23] Gomberg, M., and Sullivan, F. W., *J. Amer. Chem. Soc.*, **44**, 1820 (1922).
[24] Geddes, J. A., and Kraus, C. A., *Trans. Faraday Soc.*, **32**, 585 (1936).

Discussion

Dr. W. BECKMANN: Can you explain the high value of the activation energy of dyeing in the region 80–130°C?

Dr. FEICHTMAYR: The activation energy of dyeing is more or less the same as the activation energy of dye diffusion. Diffusion of dye in the fibre is by far the slowest reaction involved in the whole process of dyeing, and it thus governs the kinetics of the process. If the fibrous material is homogeneous in respect of the interaction between dye and fibre, the activation energy of diffusion can be defined as follows: it is the energy required to form a sufficiently large hole in the fibre near the dye molecule to permit a location change of the incorporated dye molecule (see Barrer, R. H., *Trans. Faraday Soc.*, **35**, 644 (1939); Patterson, D., and Sheldon, R. P., *ibid.*, **55**, 1254 (1959)).

With polyacrylonitrile, however, the conditions are different. Dyeing of this material is clearly based on a specific interaction between the dye cations and the anionic groups in the fibre. The dye molecule does not, therefore, move along an equipotential surface when it migrates from anion to anion. We believe, therefore, that the relatively high activation energy of dyeing of polyacrylonitrile with cationic dyes (approx. 70 kcal/mole) reflects not only the "process of hole formation" but also the potential curve between these centres of high affinity.

The activation energy of dyeing of polyester fibre with disperse dyes may serve as a comparison. This activation energy should be lower than that for polyacrylonitrile, since the system polyester–disperse dye is homogeneous with regard to the interaction between fibre and dye. The process of hole formation should, therefore, be the sole factor determining the activation energy. The studies of Patterson and Sheldon show that the activation energy of this dyeing process, 50 kcal/mole, is, in fact, considerably lower.

Dr. R. MCGREGOR: Were the measurements of physical properties made on dry material or on material which contained moisture? This may be important in view of the known effect of moisture on the physical properties of other substrates.

Dr. WÜRZ: The data on the physical properties of individual high polymers given in our paper have been taken from the literature. We know, however, that the measurements were made on dry material (private communication from K. Schmieder).

The moisture content of polyacrylonitrile should have hardly any influence on the physical properties. If the maximum molar amount of water absorbed is divided by the number of polar (CN) groups present, it is obvious that there is no specific interaction between CN and H_2O.

With polyamide fibres, the situation is different. A comparison of the maximum molar amount of water absorbed by this fibre with the number of polar (acid amide) groups present shows that the two values are of the same order. Since the water molecules in this fibrous material attach themselves in clusters to the acid amide groups, in many cases probably with rupture of the hydrogen bonds (C=O···H···N) between neighbouring chain molecules, the cohesive forces in the fibre are changed substantially. It is not surprising, therefore, that the physical properties of polyamide fibres are strongly affected by the moisture content (see Illers, K.-H., *Makromol. Chem.*, **38**, 1968 (1960)).

Mr. H. R. HADFIELD: The authors have shown that certain solvents reduce the second-order transition point of acrylic fibres. There is evidence that in the dyeing of polyester fibres the action of so-called carriers is to reduce the second-order transition point. No suitable carriers are available for unmodified acrylic fibres and it is suggested that the reason for this is that the solvents which lower the transition point of the fibre are powerful solvating agents for the dye. Would the authors agree with this view?

Dr. WÜRZ: We have pointed out in the paper that copolymerisation can shift the glass-transition interval to lower temperatures. Copolymerisation can therefore be regarded as internal plasticisation. This question concerns the external plasticisation of the fibres by *carriers*. Recent investigations into the action of carriers (see Würz, *Melliand Textilber.*, **42**, 913 (1961)) show that the glass-transition interval of polyester fibres is increased by drawing or stretching of the fibre. Carriers reduce the glass-transition interval again, thus offsetting, to some extent, the effect of drawing. This explanation apparently does not apply, however, to all carriers.

In the case of polyacrylonitrile fibre, the glass-transition interval is not affected by drawing. For this reason, the drawn fibres can be dyed at temperatures below 100°C in a finite time. If, despite this, carriers are to be used to increase the rate of dye uptake, only compounds which are strongly polar should be employed, e.g. dimethyl formamide and ethylene carbonate. When mixed with water in certain proportions, these products may act as plasticisers. The aqueous phase would probably have to contain a high proportion of organic components, and this would certainly

influence the position of the dyeing equilibrium. Special investigations would have to be carried out for each individual dye to determine how strongly this equilibrium is shifted in the direction of solution, because the solvation conditions for the ions of the dye salt are dependent on several factors.

Mr. HADFIELD: Have the authors considered using flexual rigidity as a means of examining the effect of solvents on the external structure of acrylic fibres?

Dr. WÜRZ: We have not carried out any physical measurements on polyacrylonitrile fibres treated with solvents.

Mr. G. H. CRAWSHAW: I should like to point out another disadvantage associated with the use of carriers. The second-order transition point of acrylic fibres is already rather low, and above it the fibres are very plastic. Because of this, great care is required in order to ensure that yarns and fabrics are not physically distorted when being dyed. Carriers have already been referred to as plasticisers; we have found that some carriers do indeed act as plasticisers for acrylic fibres, lowering the second-order transition point and increasing the difficulties of handling the material. Do the authors agree that this effect is likely to be general?

Dr. FEICHTMAYR: The distortion resistance of the whole polyacrylonitrile fibre (oriented and amorphous regions) depends on the plastic behaviour of the amorphous regions. It is to be expected, therefore, that any carrier which acts as a plasticiser, i.e. shifts the glass-transition interval to lower temperatures, also shifts the "plasticity limit" similarly. The ideal carrier for polyacrylonitrile dyeing would, therefore, have no plasticising effect at all. It is an open question, however, whether any such substance exists.

Dr. MCGREGOR: Have any measurements been made of the activation energy of diffusion in acrylic fibres above and below the second-order transition point?

Dr. FEICHTMAYR: Glenz and Beckmann have pointed out that the activation energy of dyeing of Dralon with cationic dyes at 80–130°C is approx. 70 kcal/mole. As the diffusion of the dye into the fibre is the slowest reaction in the whole dyeing process, this value can be regarded as the activation energy of diffusion above the glass-transition interval. We do not know of any measurements which have been made of the activation energy of diffusion below this interval.

Dr. BECKMANN: In contrast with the dyeing of polyester fibres, carriers for increasing the rate of dyeing of acrylic fibres are usually not necessary, because the rates of dyeing near the boil are much higher than those of polyester fibres. In many cases the rate of dyeing is so high that a retarder is necessary.

Dr. PATTERSON: Have the authors been able to find any direct connection between the loss peak at 105°C and 5 c/s shown in Fig. 3(*a*) and any molecular process in the fibre structure allowing the diffusion of dye molecules within it?

Dr. WÜRZ: The loss peak at approx. 100°C is due to the fact that the molecular chains become mobile at this temperature. The results hitherto obtained do not indicate whether the location changes are confined to the amorphous regions or also occur in the oriented zones.

Mobility of the molecular chains is an essential condition for activation energy (see Fig. 2), and thus for the diffusion of dye into the fibre. The close connection between chain mobility and dye diffusion can also be demonstrated by using a concept derived from Barrer (see reply to Dr. Beckmann's first question). The chain molecules must be so mobile that they form a sufficiently large hole near the dye to permit migration of dye as a result of the concentration gradient.

Dr. Ing. H. C. A. VAN BEEK: If the activation energy required for diffusion of dyes in the polyacrylonitrile fibre is high at room temperatures, as illustrated in Fig 2, would this explain the high light fastness of certain dyes on acrylic fibres? As has been shown on several occasions, fading of dyes proceeds by reaction of the dye with substances or groups present in the substrate. The high light fastness of certain dyes on acrylic fibres may be mainly due to the unreactivity of the substrate but perhaps also partly to the slow diffusion of active agents.

Dr. FEICHTMAYR: It is feasible that the high light fastness of basic dyes on polyacrylonitrile fibres is due to several factors, including (*a*) chemical inertness of polyacrylonitrile fibre to basic dyes in the original and in the light-excited condition, and (*b*) exceptionally small coefficients of diffusion of the dye molecules below the glass-transition interval.

We are convinced that factor (*a*) is of decisive importance. It can be assumed that it is the diffusion not of the activated dye molecule but of atmospheric oxygen within the fibrous material that is mainly responsible for the photochemical decomposition of the dye molecules. Numerous investigations have clearly shown that photochemical destruction of dyes occurs only when oxygen is present. We also know from the studies of Schulz and Gerrens that appreciable diffusion of oxygen is possible in high-molecular substances, even below the glass-transition interval. We are therefore led to conclude that the chemical reactivity of the substrate is of decisive importance for the light fastness of dyeings.

WEDNESDAY AFTERNOON, 20th SEPTEMBER 1961

Chairman—Mr. J. PITTARD

Coloration of Plastics, with special reference to Polyolefins

C. MUSGRAVE

An attempt is made to summarise the general properties of plastics colorants and to suggest which class is most likely to yield satisfactory results in particular plastics. Because of the growing importance of polyolefins, the coloration of these polymers is dealt with in greater detail. Dispersibility, stability to processing (heat stability), chalking, light fastness, and toxicity must all be taken into consideration in the selection of suitable colorants.

Introduction

In the wide variety of industries where colour is used, problems arise which are common to all, e.g. brilliance, hue, permanence in the end-product, and price. In addition, many problems in the coloration of plastics are created by the conditions required for their processing and fabrication.

The vast majority of plastics are coloured either with pigments, which disperse, or dyes, which dissolve in the plastics mass during compounding. The temperature and time of compounding may vary from a few minutes at 100°C for casein to 30 min at 300°C for certain polyolefins. Moreover, the environment is seldom chemically inert, and acid, alkaline, oxidative, or reducing conditions may exist or develop owing to the thermal breakdown of the system. The combined effects of time, temperature, and reactive medium frequently lead to marked colour changes in the colouring matter, or even to its complete breakdown. The degree to which a colorant withstands these conditions is termed its "stability to processing" or, more simply but less accurately, its "heat stability".

Thermoplastics of the flexible type, e.g. polyolefins and plasticised polyvinyl chloride (pvc) cannot be satisfactorily coloured with soluble dyes since these tend to crystallise in the mass on cooling and ageing. This leads to the appearance of crystals of colorant on the surface of the plastics (a phenomenon known as chalking, blooming, or crocking), or to bleeding of the dye from the plastics into material with which it is in contact (generally called migration or bleeding). Many pigments having negligible solubility in plastics systems at room temperature are much more soluble when the temperature is raised during compounding, and chalking or migration may still occur. The severity of such effects depends on the colorant, the temperature of compounding, and the nature and formulation of the medium.

In the early days of the industry, the mass coloration of plastics was fairly simple since the existing products, namely casein and celluloid, were not subjected to high-temperature processing. Hue and light fastness were the main criteria of acceptance of a colorant, and it was possible to satisfy them by selecting from existing textile dyes those cellulose acetate dyes which disperse well in solvents and water. The advent of the phenolic plastics, processed at temperatures in the region of 170°C and in conditions of considerable chemical activity, first drew attention to the need for "heat-stable" colours. The subsequent development of plasticised pvc and later of the polyolefins highlighted the hazards of colour chalking and migration. Studies of these problems revealed the marked influence of compound formulation on colorant stability, in particular light fastness, not only during processing but also in service life.

Since compound formulations, environmental conditions, and compounding and processing temperatures are almost infinitely variable, the basic problem of colouring plastics is highly complex; thus it is not possible to present even a small range of colorants which are universally applicable. On the other hand, workers in this field have gradually built up a knowledge of these factors for individual plastics, and this knowledge, coupled with an understanding of the chemical constitutions of the various dyes and pigments available, makes it possible to reduce the preparatory work required before a selection can be made.

In this paper an attempt is made to summarise the general properties of plastics colorants and to suggest which class is most likely to yield successful results in particular plastics. Because of the growing importance of polyolefins, the coloration of these polymers is dealt with in greater detail. It cannot be too strongly emphasised that the data listed are intended as a starting point from which an initial selection can be made. It is essential to test the chosen colorant in the actual medium and under the precise conditions of compounding and fabrication that will ultimately be used in bulk production.

Classification of Plastics Colorants

Many methods of classifying colouring matters are possible, according to the application for which they are required. The simple system suggested here is designed to furnish the broadest basis for comparison between the different groups of colorants of major importance to the plastics industry; therefore, no mention is made of groups of lesser potential use, e.g. reactive dyes and pigments produced by reaction of basic dyes with complex inorganic acids (complex toners). Colouring matters are initially divided into two groups, dyes and pigments.

DYES

Dyes are colorants that are soluble in the plastics system. These may be conveniently divided into three sub-groups, namely acid, basic, and solvent-soluble.

Acid Dyes

This sub-group comprises water-soluble acid wool dyes and includes many that are fairly soluble in alcohol, e.g. Orange II (C.I. Acid Orange 7) and Erioglaucine Supra (C.I. Acid Blue 1). Acid dyes are generally resistant to dilute acids, alkalis, and reducing agents and, with certain exceptions, will withstand fairly high temperatures. They give reasonably bright hues but have the defects that they bleed from the plastics into soap and detergent solutions and may be extracted with solvents. Since they are not substantive to most plastics, their properties in these media cannot be related to their properties on wool. This is particularly true of light fastness since, almost without exception, the acid dyes have poor light fastness in plastics. Nevertheless, water-soluble acid dyes are used for the mass coloration of casein and the alcohol-soluble ones for phenolic plastics, where their indifferent light fastness is of minor importance, owing to the fugitive nature of the base.

Basic Dyes

Basic dyes form a well-known class of wool dyes of very high brightness and intensity. They are highly soluble in alcohol, which would suggest useful applications in several plastics. Unfortunately, heat stability and light fastness are generally inadequate, and only Methyl Violet (C.I. Basic Violet 1), Victoria Blue B (C.I. Basic Blue 26) and the Rhodamines (e.g. C.I. Basic Violet 10, C.I. Basic Red 1) are used to any marked extent. The blue and violet dyes are satisfactory shading components for black phenolic plastics, whilst in these media bright bluish reds are obtained with the Rhodamines. Rhodamines are also used in cellulose acetate and nitrate plastics, since they are unequalled in brightness and fluorescence.

Solvent-soluble Dyes

This group comprises a variety of dyes of widely differing chemical composition, ranging from the simple monoazo hydrocarbon-soluble dyes, e.g. Fat Orange R (C.I. Solvent Yellow 14) to the more complex anthraquinonoid dyes, e.g. C.I. Solvent Blue 21. They possess good to excellent heat stability, especially in less chemically reactive polymers (e.g. polystyrene) and find considerable favour in the crystal grade for the production of transparencies. They should not be used in plasticised pvc or the polyolefins, since bleeding or chalking will inevitably occur.

The alcohol-soluble Nigrosines (e.g. C.I. Solvent Black 5) and Indulines (C.I. Solvent Blue 7) are very important members of this group, being extensively used for blacks in phenolic and cellulosic plastics. They are not, however, considered satisfactory for polystyrene since they give rise to surface blemishes on the finished moulding, an effect known as "fish scaling". Several of the solvent-soluble dyes are used for colouring polyester resins. Careful selection is necessary, since most soluble dyes interfere with the hardening characteristics of the resin.

PIGMENTS

Pigments are of immense value to the plastics industry since they are used to colour at least 90% of all coloured plastics. They can be divided into two main groups, inorganic and organic.

Inorganic Pigments

These are opaque, of high density and of limited colour range. In comparison with organic pigments, they are rather dull and rapidly lose both strength and brightness on reduction with white pigments. Although not generally resistant to chemical attack by acids and alkalis, they are very stable to heat in inert systems and, except in certain special cases, very fast to light. Inorganic pigments may be further subdivided as follows—

Chrome Pigments

Chrome pigments provide a range of yellows (C.I. Pigment Yellow 34) and oranges (C.I. Pigment Orange 21) of good but not outstanding heat stability. They tend to darken on exposure to daylight and, being based on lead, may be attacked by sulphur when exposed in industrial atmospheres. They are rapidly attacked by alkalis and therefore are not widely used for colouring heavily filled vinyl flooring compounds. Since they are insoluble in esters, hydrocarbons, ketones, etc., they may safely be used in plasticised pvc and polyolefins without risk of chalking or migration. They are also used for colouring cellulose, acrylic, and polystyrene plastics.

Cadmium Pigments

The yellow (C.I. Pigment Yellow 37), orange (C.I. Pigment Orange 20) and red (C.I. Pigment Red 108) regions of the spectrum are spanned by the cadmium sulphides and sulphoselenides. They have excellent heat stability and very good fastness to light, although the yellow bleaches rapidly on exposure in moist atmospheres when reduced with white pigment. They are insoluble and chemically inert, except in presence of acids, and form a most versatile range of plastics colorants, being extensively used in pvc, polystyrene, and polyolefins. Their main disadvantage is their lack of tinting power (about 20% of that of organic pigments), which makes their use rather costly.

Ultramarines

The ultramarines are notable as bright reddish blues. Being calcined products, they have excellent heat stability but are sensitive to acids, and a tendency for the free sulphur to react with stabilisers in pvc plastics may result in change of hue during processing in these systems. The principal disadvantage of the ultramarines is their low tinctorial strength.

Iron Oxides

The colours of the natural and synthetic iron oxide pigments range from yellow to red, brown,

maroon, and even black. They are dull and tinctorially very weak but are cheap. Heat stability and light fastness are excellent in most systems, but degradation of pvc tends to occur unless large amounts of stabiliser are present. For this reason, they cannot be recommended for application to polyvinyl plastics, although they are often used with success in vinyl flooring. They are particularly attractive in phenolic moulding materials for the production of inexpensive browns.

Organic Pigments

Organic pigments provide an extensive range of bright, transparent colours of high tinctorial strength. They are generally more resistant to chemicals but less stable than inorganic pigments and, although there is an ever increasing number of exceptions, less fast to light. From the large number available, the following classes are of interest to the plastics industry.

Entirely Organic Pigments

These are monoazo, disazo, and polyazo pigments free from metals and sulphonic and carboxylic acid groups.

Typical monoazo pigments are Toluidine Red (C.I. Pigment Red 3), arylamide yellow (C.I. Pigment Yellow 1) and BON/arylamide red (C.I. Pigment Red 7). The good light fastness of these pigments is not matched by their resistance to high temperatures and they can seldom be processed in plastics above 170–180°C without suffering breakdown. They are all soluble to varying degrees in thermoplastics, e.g. pvc, cellulose acetate, and polyolefins, and hence chalking or migration occurs. Because of their strength, brightness, light fastness and comparatively low cost, they are widely used for colouring phenolic, urea, and melamine plastics.

The more important members of the disazo pigments are the yellows, oranges, and reds based on dichlorobenzidine, e.g. C.I. Pigment Yellow 13, C.I. Pigment Orange 13, and C.I. Pigment Red 38. Their heat stability is far superior to that of the monoazo pigments and, because of their higher molecular weight and greater complexity, they are less soluble in organic solvents. They can therefore be used in plasticised pvc, cellulose acetate, and polyolefins, although the less complex members (e.g. C.I. Pigment Yellow 12) migrate rather heavily when incorporated at low concentration in plasticised pvc. Light fastness in most plastics is adequate, except when pastel shades are required. Monoazo pigments are preferred for thermosetting plastics on economic grounds.

The few available (red–maroon) polyazo pigments show better heat stability and light fastness than the monoazo and disazo types, although they are somewhat less bright. They find increasing use in high-temperature-processed polyolefins and polystyrene, and are of special interest where pastel shades of good light fastness are required.

Metal Toners

Toners (in this classification) are heavy-metal (Ba, Ca, Mn) salts of sparingly water-soluble azo dyes prepared without a substrate. They are strong and bright, and generally have good fastness to heat, but not to alkali. The most important ones for application to plastics are the Barium, Calcium, and Manganese 2B Toners (C.I. Pigment Red 48), Barium Lake Red C (C.I. Pigment Red 53), Calcium 4B Toner (C.I. Pigment Red 57), and two yellows, Irgalite Yellow WSC (Gy) and Irgalite Yellow WSR (Gy), of unpublished constitution. Light fastness, which varies appreciably from toner to toner, is highest for the yellows. The Calcium and Manganese 2Bs, although somewhat less stable, are adequate for most applications, but Calcium 4B and Barium Lake Red C are rather fugitive, especially if used at low concentration.

Because of their low solvent solubility, toners do not migrate or chalk and, having the added advantage of low cost, are used widely in both thermoplastic and thermosetting systems, e.g. phenol–formaldehyde, pvc, polyolefins, polystyrene, and acrylics.

Metal Complexes

In metal complexes the metal is chelated instead of forming a salt as in metal toners— its purpose is to give stability toward heat and solvents. The members of this group are relatively few and will be discussed individually.

Pigment Green B (C.I. Pigment Green 8) This is the well-known iron complex of α-nitroso-β-naphthol. It has high tinctorial strength and, because of its solvent fastness, is non-chalking and non-migratory in plasticised media. Heat stability is, however, only moderate, especially at low concentration, and the pigment will seldom withstand the temperatures required for processing polyolefins. It is used fairly widely in pvc, but its iron content can lead to polymer breakdown on prolonged exposure, unless the stabiliser content is high. Its high strength and low cost make it an attractive pigment where temperature conditions permit.

Nickel-azo Yellow (C.I. Pigment Green 10) A green–yellow pigment of only moderate tinctorial strength, when compared with most organic pigments, nickel-azo yellow has outstanding light fastness, except in urea– and melamine–formaldehyde resins. It is fast to solvents, and non-chalking and non-migratory in pvc. Heat stability is good but not quite adequate to meet the highest temperatures encountered in processing some plastics, e.g. in the pin-point injection moulding of polystyrene. Its use in plastics is limited more by its unusual colour than by any lack of technical performance.

Phthalocyanine pigments The phthalocyanines are unique. An extremely stable chemical configuration gives very good fastness properties, which are enhanced by formation of the copper complex. Blues produced in this way are standard pigments throughout the plastics industry. They possess outstanding light fastness, even when heavily reduced with white pigments, and, provided the correct crystal type is selected for a given plastic, excellent heat stability. Absence of migration or chalking, and excellent resistance to solvent extraction, are further desirable features. The main disadvantages are the difficulty of

dispersing them (now virtually eliminated by recent developments) and their poor resistance to oxidising agents. The latter property may influence their behaviour in polyester resins where oxidising catalysts are required, resulting in a change of colour of the pigment or increase in hardening time.

Chlorination of copper phthalocyanine produces a range of greens whose technical properties are roughly similar to those of the blues. Heat resistance and freedom from defects due to solvent solubility are characteristic, and light fastness is generally of the same high order as that of the blues. An exception is in formaldehyde-containing systems, e.g. urea and melamine plastics, where, although the colour is not altered during hot processing, there is a distinct reduction in light fastness on exposure.

Vat Pigments

Vat pigments are organic pigments of high molecular weight and compact structure, originally developed for textiles, to which they are applied as the leuco compound and subsequently oxidised to produce the pigment in the fibre. Application to plastics in this way is not possible and for this purpose they have been developed as pure pigments in the fully oxidised state. Their properties in plastics, particularly light fastness, cannot be compared with those in textiles, but from those examined a few have emerged, e.g. C.I. Vat Orange 7 and C.I. Vat Blue 20, which have the high stability required for application in plastics. They are particularly useful in acrylic and polyester resins and for giving light-fast tints and pastel colours in pvc, polyethylene, and polystyrene. They are not generally satisfactory for use in urea and melamine plastics because of the risk of reduction by formaldehyde.

Although not strictly vat pigments, the new quinacridone reds and violet can be considered under this heading, since structurally they resemble the vats and have similar compact configurations. In the crude form, like vats, they are not satisfactory colorants for plastics, but can be subsequently developed as high-stability pigments in these media. Light fastness is of the same order as that of the phthalocyanines and heat stability is also very good. The major drawback to the extensive use in plastics of the true vat pigments and the quinacridone pigments is their high cost, which automatically places them in the speciality class.

Lakes

Lakes are usually prepared from water-soluble acid dyes precipitated as a salt (usually by barium chloride) on to an inert substrate, e.g. alumina blanc fixe. They are tinctorially weak but often very bright and, if the correct acid dye is selected, fast to solvents. They have two major defects, moderate light fastness and poor alkali fastness. Heat stability is usually very good, and migration and chalking in plasticised systems seldom occur. Lakes were widely used in the early days of plastics but have now been superseded by more permanent pigments of high tinctorial strength. An interesting lake, which is used in polystyrene, polyolefins, and pvc, is violet lake (C.I. Pigment Violet 5).

Table I summarises the general properties of plastics colorants. Since the behaviour of a colouring material depends not only on the colorant itself but also on the medium, temperature, and time of compounding, the table should be regarded only as a guide.

Coloration of Polyolefins

The largest growth factor shown by any plastics materials during the last ten years is probably that of the polyolefins. Almost the whole of the early U.K. production was consumed by the packaging and electrical industries, the majority of it uncoloured. More recently, the advantages of the polyolefins for domestic articles and toys have been realised, and now in the U.K. almost 40% of polyolefin production is ultimately marketed in a coloured form. If this is viewed against the anticipated sales of 160,000 tons in 1961, it will be seen that the technology of polyolefin coloration is of major importance.

The ideal pigment for colouring polyolefins should be easily dispersed, stable to processing, and of the colour and properties demanded by the end-use. As it is not always possible to achieve the ideal, some compromise has often to be made when selecting colorants. Usually, the best that can be achieved is to select a pigment which will function satisfactorily under a certain set of conditions.

When considering the more common properties which a colorant for polyolefins should possess, one should bear in mind that many will depend upon the specific end-use, and it is therefore not possible to assign priorities. On the other hand, dispersibility, resistance to heat, and freedom from exudation and chalking must be considered as fundamental, irrespective of the application. These properties, together with fastness properties and toxicity, will now be discussed.

DISPERSIBILITY

The ease with which the dry, powdered pigment can be dispersed in a polyolefin depends on (*a*) the pigment, (*b*) the polymer, and (*c*) the equipment.

Effect of Pigment

Pigments which disperse best are those of small particle size and soft texture. Certain organic pigments have low melting points and a tendency to dissolve in the polymer. Although this undoubtedly assists dispersion, it gives rise to chalking. Some pigments of correct texture and particle size tend to agglomerate when compressed. These agglomerates may fail to break down during the compounding cycle and hence not disperse adequately.

Effect of Polymer

Polymers with high melt index make pigment dispersion difficult, since they become very fluid at working temperatures and there is therefore little shear on the pigment aggregates. Low-pressure

TABLE I

General Properties of Plastics Colorants

Colorant	Tinctorial strength	Brightness	Chemical stability	Solubility characteristics	Migration Chalking	Heat stability	Light fastness	Recommended plastics*	Remarks
Acid dyes	strong	bright	satisfactory	water	—	very good	moderate/ poor	casein p–f	
Basic dyes	very strong	very bright	satisfactory[1]	water/alcohol	—	poor	poor	p–f c.a. c.n.	[1] greens attacked by reducing agents
Solvent-soluble dyes	strong	bright	satisfactory	alcohol/h.c.	migration	very good/ excellent	moderate/ excellent	p–f p.s. c.a. c.n. p.est	do not use in pvc or p.c.
Chrome pigments	weak	moderate	sulphur sensitive alkali sensitive	insoluble	none	good	moderate[2]	pvc p.c. p.s. c.a. ac	[2] may darken on exposure
Cadmium yellow	weak	fairly bright	acid sensitive	insoluble	none	excellent	excellent[3]	pvc p.s. p.o. u–f m–f c.a. c.n. ac	[3] except with TiO_2 in moist conditions
Cadmium reds/ maroons	weak	dull	acid sensitive	insoluble	none	excellent	excellent	pvc p.s. p.c. u–f m–f c.a. c.n. ac	
Ultramarines	very weak	fairly bright	very acid sensitive	insoluble	none	excellent	excellent	c.a. c.n. pvc p.o.	
Iron oxides	very weak	very dull	satisfactory	insoluble	none	excellent[4]	excellent[4]	p–f u–f m–f	[4] may degrade pvc polymer
Monoazo pigments	strong	bright	satisfactory	slightly h.c. soluble	chalking[5] migration	poor/ moderate	very good	casein p–f u–f m–f p.est	[5] not suitable for use in plasticised pvc
Disazo pigments	strong	bright	satisfactory	insoluble	none[6]	very good	good/ very good	pvc p.o. c.a. c.n. p.est p.s.	[6] less complex members may migrate
Polyazo pigments	strong	fairly bright	satisfactory	insoluble	none	very good/ excellent	very good	pvc p.o. p.s. p.est[7] c.a. c.n.	[7] use limited by rather high cost
2B toners	strong	bright	alkali sensitive	insoluble	none	very good	moderate/ good[8]	p–f pvc p.s. p.o. c.a. c.n.	[8] Mn salt has highest light stability
4B toners	strong	bright	alkali sensitive	insoluble	none	moderate	moderate	pvc p–f p.o. c.a. c.n.[9]	[9] when processing temperatures are low
Barium Lake Red C	strong	bright	alkali sensitive	slightly h.c. soluble	migration	excellent[10]	poor	p.s. p.o.	[10] in crystal p.s. and p.o.
Iron α-nitroso-β-naphthol	very strong	dull	satisfactory	insoluble	none	moderate	good	p–f pvc[11]	[11] may cause pvc degradation
Nickel-azo yellow	moderate	fairly bright	satisfactory	insoluble	none	very good	excellent	p.o. p.s. pvc c.a. c.n.	
Phthalocyanine blues	strong	bright	satisfactory	insoluble	none	excellent[12]	excellent	all plastics	[12] provided correct grade is selected
Phthalocyanine green	strong	bright	satisfactory	insoluble	none	excellent	excellent[12]	all thermoplastics	[12] poor in u–f and m–f
Vat pigments (and quinacridones)	strong	moderate	satisfactory[14]	insoluble	none[15]	excellent	excellent	all thermoplastics	[14] poor in u–f and m–f
Lakes	weak	bright	alkali sensitive	insoluble	none	very good	poor/ moderate	p.s. p.o. pvc	[15] some show slight migration; these are being replaced by stronger and more stable pigments

* Abbreviations used for plastics are as follows—

p.o. = polyolefin; p.s. = polystyrene; pvc = polyvinyl chloride; p.est = polyester resins; h.c. = hydrocarbon; p–f = phenol–formaldehyde; u–f = urea–formaldehyde; m–f = melamine–formaldehyde; c.a. = cellulose acetate; c.n. = cellulose nitrate; ac = acrylic

high-melt-index polyethylene and polypropylene are particularly difficult in this respect.

Effect of Equipment

Great improvements in the dispersion of pigments can be achieved by correct choice of compounding, extrusion, and injection moulding machinery, the aim being to create the maximum turbulence and hence shear on the pigment particles. Two main methods of colouring polyolefins are in general use, mass coloration and dry tumbling. In the former method a dry premix of pigment and polymer is prepared and then compounded, by a hot compounding cycle in an internal mixer, on the open rolls or in an extruder. The homogeneous product is next ground or diced and subsequently moulded or extruded into the finished form. Reasonable dispersion can be obtained with some organic pigments by this method, but many others, e.g. the phthalocyanine blues and greens, do not always give speck-free end-products. Certain carbon blacks, cadmium pigments, and ultramarines also give inadequate dispersion by such means. Where problems of this type arise, it is usual to prepare a highly concentrated masterbatch of pigment and polyolefin, whereby much greater shear can be applied and better dispersion obtained. The masterbatch is then diced and added to virgin polymer; a second compounding follows, and, finally, injection moulding.

The disadvantages of adopting a masterbatch technique are that the method is rather cumbersome and costly and there is a considerable risk of contamination from flying particles of colour. Perhaps the biggest disadvantage, however, is that the pigment is subjected to an extra heat cycle which may considerably lower its ultimate stability, since pigment degradation depends on both time and temperature. The polymer also may be partially degraded by the extra heat treatment: this is particularly true of polypropylene. The masterbatch technique itself, however, is a means of ensuring good dispersion and is widely used at present.

In the second method of colouring polyolefins, dry tumbling, the pigment and polymer granules are tumbled together, sometimes in the presence of a small quantity of a dispersing agent, until the polymer granules are smeared with an even coating of colorant. The granules are then injection moulded or extruded. The mouldings obtained by this process will seldom withstand close inspection by transmitted light. Specks of undispersed pigment are usually noticeable. Because of poor dispersion, full colour yield from the pigment is not obtained and, when changes are made from one piece of equipment to another, differences in hue invariably occur. Poor dispersion is also one of the main causes of the poor electrical properties of coloured polyolefins.

Mechanical methods for improving dispersion have been developed and some have had reasonable success— these usually require the incorporation of a screen, torpedo, or venturi plate in the extruder or injection machine. Colorant manufacturers have also been tackling this problem, the object being to produce pigments of fine particle size and soft texture which will not aggregate during the compounding process, and some success has been achieved.

STABILITY TO PROCESSING (HEAT STABILITY)

The heat stability of a colorant depends upon several factors, including heating time and temperature, and the grade of polymer. Times and temperatures vary over a very wide range according to the type of polyolefins being processed and the nature of the end-product; high-pressure low-density polythene, for instance, may be extruded at temperatures as low as 180°C with a maximum time of heating of 10 min, whereas polypropylene monofilament may be heated to 300°C and above for up to 30 min. Again, although the polyolefins are basically inert, they occasionally contain reactive residues of catalysts and usually some antioxidant. The nature of the residues and the antioxidant will vary from polymer to polymer and from one source of manufacture to another; hence, it must not be assumed that the stability of a selected colorant will remain constant irrespective of polymer change. Also, the temperature of the plastics mass will be different in one type of compounding equipment from that in another, owing to differences in frictional heat. It is essential, therefore, that the heat stability of a colorant be checked in the same polymer and under the exact processing conditions that will apply in bulk production.

CHALKING

It is believed that colour chalking in polyolefins is caused in the same way as in unplasticised pvc, i.e. the pigment dissolves during hot compounding and, on cooling, forms a supersaturated solution, which results in crystallisation; microscopic examination of the surface of the plastic reveals the presence of crystals of the pigment.

The phenomenon of chalking is restricted almost entirely to organic pigments, and it is found in practice that those pigments which chalk in pvc will invariably do so in polyolefins, usually to a much smaller degree. The rate at which chalking becomes visible is influenced by the temperature of compounding and also by exposure to daylight— the latter accelerates chalking from polyolefin plastics. All monoazo organic pigments (i.e. those that do not contain metal, or sulphonic and carboxylic acid groups) are highly susceptible to chalking.

LIGHT FASTNESS

The importance of this property depends entirely on the end-use of the plastic. Certain products, e.g. toys, require only sufficient light fastness to keep them from fading during display, since they are seldom exposed to direct sunlight for long periods. On the other hand, clothes lines, refuse bins, etc., require a very high degree of light fastness.

Generally speaking, the requirements of the industry can be met with existing inorganic or organic pigments, with the possible exception of the reds. In terms of *BS* 1006:1955, a rating of 5–6

is adequate for all applications except those requiring maximum light fastness. In these cases ratings of 7 or 8 are desirable. As with other plastics, the light stability of the colouring material in polyolefins varies directly with the amount of colorant present and inversely with the amount of white pigment. Because the polyolefins are resistant to moisture, the light fastness of many pigments in these media is enhanced.

The inclusion of ultraviolet absorbers, primarily to stabilise the polymer, may also have an effect on the light fastness of the colorant; this will depend on the specific wavelengths which bring about fading of the pigment. If fading is induced by visible light, an ultraviolet absorber will have no beneficial effect, but if ultraviolet radiation is the source of colour degradation, its inclusion is worth while.

TOXICITY

The problem of toxicity is extremely complex, particularly when applied to pigments. There is no single authority in the United Kingdom which can indicate whether a pigment can be used in contact with foodstuffs, e.g. for the packaging industry. The British Plastics Federation published, in 1958, a report of the Toxicity Sub-Committee of the Main Technical Committee which threw some light on this problem and made certain recommendations. Two factors were considered, the toxicity of the additive and the amount of that additive extracted by certain extracting fluids, and as a result of the work a quantity, Q, the toxicity quotient, was defined.

$Q = 1000E/T$ where E is the amount of obnoxious substance extracted from the material and T is the toxicity factor of the extracted material in any authoritatively given figure in mg per kg of body weight. It was agreed that an arbitrary figure of less than 10 for each ingredient should be the standard of non-toxicity for any plastic. However, the following reservations were made—

(*a*) that a Schedule 1 poison should not be included in the plastics material,

(*b*) that additives should not contaminate the foodstuff with a material considered obnoxious in law,

(*c*) that any heavy-metal contamination from the additive should not raise the heavy-metal content of the foodstuff (allowing for that already present in the foodstuff) beyond any limit prescribed by the Ministry of Food.

The report also dealt with substances which may have carcinogenic effects as follows—

"The procedure should be that any substance to which the stigma of carcinogenisis might be attached should be discarded. Other substances can be assumed to be innocent but tests to prove this innocence are not worth while."

Because of the great difficulties of measuring small traces of poisonous heavy metals which may be extracted from the plastic when, e.g., the lead-based pigments are used, it is advisable to omit pigments of this type from the range of colorants which may come in contact with foodstuffs. The selection of pigments for such applications should therefore be made as follows—

(1) The initial selection should be made from—

(*a*) organic pigments which do not contain any known carcinogenic substances,

(*b*) metal toners of the calcium and manganese types, but not barium salts,

(*c*) metal-complex pigments,

(*d*) vat pigments which do not contain any known carcinogenic groupings,

(*e*) lakes, where the inert substrate is of the alumina type.

(2) Chosen pigments should be examined for all aspects of heat stability, dispersion, light fastness, etc., and those which pass submitted to colour extraction tests.

(3) Colours acceptable under (1) and (2) should be incorporated in the polymer under the precise conditions and at the concentration intended to be used in practice, and immersed in extracting fluids. Where possible, these fluids should be of the type with which the coloured polythene will ultimately come in contact, but when such fluids are already coloured it may be necessary to substitute a similar but colourless extracting medium. If any bleeding of the colouring material into the extracting fluid is observed then such colours should be rejected.

PLASTICS CHEMICALS DIVISION
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(*MS. received 20th April 1961*)

Discussion

Mr. H. R. HADFIELD: Mr. Musgrave mentions the deleterious effect of titanium dioxide on the light fastness of many dyes. Many processes have been proposed, and confirmed, which reduce considerably the catalytic effect of TiO_2, and these depend, in effect, on the poisoning of the TiO_2 catalyst with very small amounts of Co, Cr, or Mn salts. So far as I am aware these processes have been suggested for fibres only. Have they been extended to plastics materials?

Mr. MUSGRAVE: To the best of my knowledge these processes have not been extended to plastics materials. This could be explained for pvc plastics by the fact that Cr in some forms is considered to act as a catalyst for the breakdown of pvc. In addition, Mn salts, in many pvc polymers, darken on prolonged exposure to light, owing, it is believed, to the formation of manganese dioxide.

Mr. R. K. FOURNESS: The example of pigment migration—a yellow in pvc—shown in which the degree of migration reached a maximum and then decreased with increasing depth of colour was both interesting and surprising. Has Mr. Musgrave any explanation to offer for this effect?

Mr. MUSGRAVE: The migration phenomenon mentioned requires a pigment which is partially soluble in the hot plasticised system and relatively insoluble in the cold. When the pigment is present at low concentrations, the particles formed on cooling can move fairly freely throughout the

mass. If the pigment concentration is high, however, flocculation occurs, so that movement is much restricted and migration less severe.

Mr. R. J. HANNAY: In the section of the paper dealing with inorganic pigments, reference is made to chrome pigments, but only to the extent of mentioning chrome yellows and oranges. These are criticised on the grounds of darkening on exposure to light and attack by industrial atmospheres. No mention is made of Chrome Oxide Green (C.I. Pigment Green 18), which is one of the most stable and light-fast pigments known. Its heat stability and resistance to attack by acids and alkalis are excellent. Is the omission of this pigment an oversight or are there some technical reasons which precluded the inclusion of this pigment as a suitable colorant for the purposes dealt with in this paper? It is known that Chrome Oxide Green is being used for the colouring of pvc.

Mr. MUSGRAVE: The omission of Chrome Oxide Green is an oversight. It can be used successfully in many plastics, although the equally stable, stronger, and brighter Phthalocyanine Greens are frequently preferred.

Mr. HANNAY: Stress is laid on the necessity of using pigments of small particle size in order to achieve good dispersion in the polymer. Does Mr. Musgrave consider this to be the main factor in relation to good dispersion, and can he give some indication of what would be considered to be the optimum particle size?

Mr. MUSGRAVE: Particle size is only one factor governing ease of dispersion—equally, or perhaps more, important is softness of texture. It is not possible to give an optimum particle size, since the ultimate pigment particles vary in size between approx. $\frac{1}{10}\ \mu$ and $\frac{1}{4}\ \mu$. These particles are, however, aggregated in the pigment powder, which may contain particles of size 1–50 μ. From the practical viewpoint, pigments for the coloration of plastics should have a soft texture and be capable of passing through a 200-mesh British Standard sieve without leaving a residue.

Mr. HANNAY: It is known that many pigments, whilst being good colorants, do give rise to "crazing" and degradation of the polymer on exposure to light and weathering. I have heard it stated that, for polyolefins, only Carbon Black is really completely satisfactory in this respect. From our knowledge of the properties of chromium oxide it is indicated that this pigment might also be highly satisfactory. Would Mr Musgrave comment further on this aspect?

Mr. MUSGRAVE: Carbon Black is undoubtedly an excellent pigment for preventing the degradation of polyolefins on exposure to sunlight. There are, however, one or two organic pigments which behave in a similar manner, e.g. Irgalite Yellow WSC (Gy) and Irgalite Yellow WSR (Gy).

Mr. L. E. JONES: Does the problem of volatility arise when dyeing plastics in bulk?

Mr. MUSGRAVE: Volatility is not a problem generally encountered when plastics are mass-coloured with pigments, because of their high melting points. When low-molecular-weight fat-soluble dyes are used, volatility problems can arise.

Mr. T. FLANAGAN: Is dichroism a serious problem in the pigmentation of plastics materials?

Mr. MUSGRAVE: No; it occurs with the phthalocyanine pigments and, of course, with certain soluble dyes, e.g. Rhodamines. In general, use is made of dichroism to yield unusual effects.

Mr. FLANAGAN: Is any difficulty experienced in the pigmentation of plastics due to inflation or "gassing"?

Mr. MUSGRAVE: Gassing due to the inclusion of pigments in plastics is not common. I have only encountered one instance during many years association with the plastics and pigments industries—the cause of this particular incident was never satisfactorily determined.

Mr. F. NORTH: On the older types of plastics, the "texture" of a pigment was a reasonable guide to its dispersibility. With polythene and, particularly, polypropylene, texture is little guide to behaviour. Mr. Musgrave mentions the tendency of pigments to form aggregates on working as being the explanation for this phenomenon. Has he any evidence to support this theory and has he any laboratory technique to determine the tendency of pigments to form hard aggregates?

Mr. MUSGRAVE: Aggregates are undoubtedly formed by the pigment being compressed against the metal parts of the mixing, moulding, or extruding equipment. In the finished product they are noticeably larger than the particles of the pigment initially introduced. I do not know of any laboratory test which will determine the tendency of a pigment to form aggregates.

Dyeing Chrome-tanned Leather with the Aid of Ethylene Oxide Levelling Agents

J. HERNDL and W. HALDEMANN

A brief description is given of the properties of leather, with particular reference to the application of dyes in presence of non-ionic, anionic, and cationic auxiliary agents. Fixation of chrome complex, vegetable, and synthetic tanning agents is described. The dyeing of suède leather is considered in detail, and the effect of two "non-ionic" polyoxyethylene derivatives on the absorption spectra of six sulphonated azo dyes is studied. It is concluded that, to obtain satisfactory dyeings on chrome-tanned suède leather, the dyes used must have similar affinity, any differences in affinity must be minimised by addition of a suitable auxiliary agent, and the agent must have similar effects on the absorption spectra of all the dyes used.

Introduction

The demands primarily made on the quality of leather dyeings include good all-round fastness, a high degree of levelness and, in the case of special types of leather, uniform distribution of the dye throughout the cross-section of the substrate. In order to meet these demands, the leather dyer has to overcome a host of difficulties, some of which are unknown to the textile dyer. The problems encountered in the dyeing of leather arise in the main from the complicated chemistry and physical structure of the skin, on the one hand, and from the various treatments it undergoes during its conversion into leather, on the other.

We shall therefore first deal with the manifold properties of leather, which will make clear the processes involved in the application of dyes to this substrate in presence of non-ionic, anionic, and cationic auxiliaries.

The animal skin contains 35% by weight of protein in the fresh state, whilst in the dry state it contains up to 95% protein [1]. The proteins include collagen, elastin, and keratins, which together constitute the fibrous portion, and glycoproteins, albumins, and globulins, which are non-fibrous proteins that do not in themselves make leather (globular or corpuscular proteins). From a technical point of view collagen is the most important protein, constituting the bulk of the fibrous portion.

The collagen fibres are composed of polypeptide chains to which a large number of polar and non-polar side-chains are attached. Comparison of the proportion by weight of polar and non-polar side-chains in collagen fibres shows that the collagen of animal skins differs substantially from the protein structure of silk, and resembles more closely that of wool (Table I) [2].

The specific charge on the polar side-chains can be made primarily responsible for the capacity of collagen to combine with various chemicals. The side-chains carry an equal number of positive and negative charges at the isoelectric point, which is between pH 5 and 7, depending on the purity of the collagen [3]. An increase or decrease in the positive or negative charge is brought about by altering the pH or by chemically masking the polar groups.

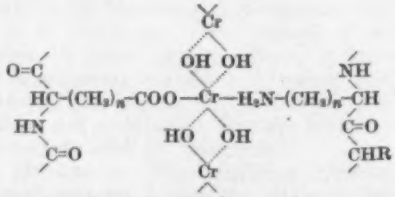
If one examines, for example, the affinity of collagen for a simple azo dye (Orange II) in relation to pH, it is observed that the fixation is distinctly reduced with a rise in pH. The anionic dye combines with the positively charged groups of the collagen. Thus, if these positive groups are discharged by decreasing the hydrogen-ion concentration, the capacity of the collagen fibre to combine with the dye is reduced accordingly.

TABLE I

Side-chain Groups of Polypeptide Structure of Various Proteins

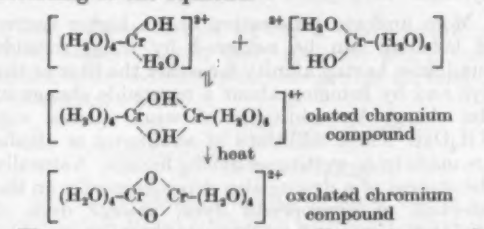
Side-chain groups	Weight of side-chains (% of total protein weight)		
	Silk	Collagen	Wool
Non-polar groups (–H, $-CH_3$, $-SCH_3$ etc.)	6·3	14·1	12·0
Hydroxyl groups (serine, hydroxyproline)	12·3	7·4	8·8
Thiol groups (cysteine)	0·0	0·0	8·0
Basic groups (amino, guanidino, imidazole)	0·6	8·0	8·0
Acid groups (carboxyl)	not available	8·4	10·8
Total of polar groups	13·1	23·8	32·5
Total of non-polar groups	6·3	14·1	12·0
Total of side-groups	19·4	37·9	44·5

It is, of course, not the charge on the untanned collagen fibre but that on the tanned fibre which determines the type of dyeing process to be employed and the results obtained [4]. Nowadays, skins and hides are mostly tanned with basic chromium complexes, and the actual tanning effect achieved depends in the first place on their capacity to unite with the protein of the skin. Küntzel [5] explains the fixation of a chrome tanning complex to the protein fibre as follows—



The optimum pH range for reaction between the collagen and the chrome compound is 2–4·5. The carboxyl groups of the protein are discharged at a lower pH so that the chrome complex cannot

react, whereas at higher pHs the basic chrome tanning salt begins to precipitate as hydroxide. During the normal course of tanning the initial chrome tanning salts form cationic linear polymers according to the equation—



These complexes substantially increase the positive charge on the untanned substrate, which explains the higher affinity of the collagen in chrome leather for anionic dyes. Fig. 1 shows the uptake of Crystal Ponceau (C.I. Acid Red 44) by chrome leather, collagen, and chromic oxide [6].

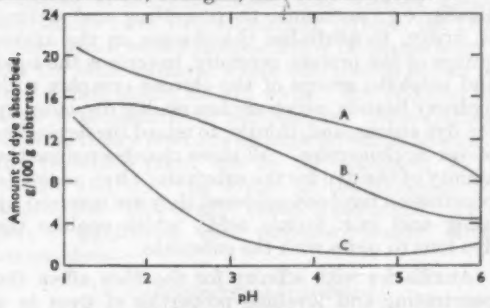
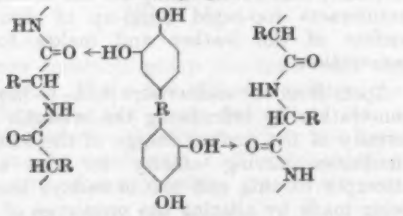


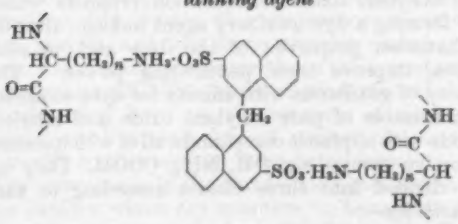
FIG. 1—Uptake of Crystal Ponceau (C.I. Acid Red 44) by chrome leather (A), collagen (B), and chromic oxide (C)

Leather which has been tanned with vegetable or synthetic tanning agents shows a dyeing behaviour completely different from that of chrome-tanned leather. Both vegetable and synthetic tannins are anionic compounds of high molecular weight which are capable of forming hydrogen bonds and electrovalent linkages with the collagen.

Linkage between collagen and a vegetable tanning agent [5]



Linkage between collagen and a synthetic tanning agent [7]



The collagen becomes negatively charged as a result of the deposition of large percentages of these tannins in the substrate, which leads to greater absorption of cationic dyes and a reduction in the affinity of the collagen for anionic products. Tanning can be effected not only with chrome salts and vegetable or synthetic tanning agents, but also with combinations of these and a number of other products. Therefore, the behaviour of leather towards dyes clearly varies according to the type of tannage which has been employed. It can thus be easily understood that this fact, together with the differences in skin structure, present difficulties of a kind usually unknown to the textile dyer. In view of the many problems involved we shall limit our discussion to one particular aspect, namely, the penetration and level-dyeing of chrome-tanned suède leather.

Suède leather is the general term for leathers whose wearing surface has been finished to have a fine velvet-like nap produced on the flesh side by abrasion. This operation, called wheeling or buffing, is usually carried out both before and after dyeing. Obviously, the leather has to be penetrated as uniformly and as completely as possible by the dye, otherwise irregularities in the dyeing become visible on wheeling. Uniform and complete penetration can in principle be ensured only if sufficient sites for the fixation of the anionic dyes have been created by an increased and even deposition of cationic chromium complexes in the skin.

As has been shown by Otto [8] in particular, the use in the tanning of suède leather of so-called masked chromium compounds, i.e. chromium salts with ligands having high complexing ability, markedly reduces the dyeability toward anionic dyes. By adding compounds of high complexing ability, e.g. oxalic acid, to the chromium salts, the cationic properties of the latter are reduced, which leads to uncharged and anionic chromium compounds. If masked anionic chromium complexes of this type are used for tanning, a corresponding negative surface charge is imparted to the treated leather, and this results in a lower affinity for anionic dyes. This is clearly indicated in Fig. 2, which shows the effect of repeated chrome tanning on the dye uptake.

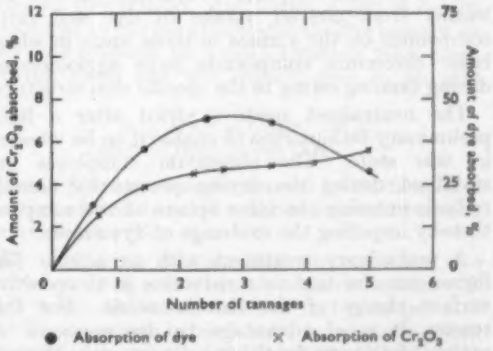


FIG. 2—Effect of repeated tannages (each with 2% Cr_2O_3 in form of masked solutions) on uptake of Cr_2O_3 and dye (0·03 mol. % Diamine Black BH—C.I. Direct Blue 2)

To produce a readily dyeable suède leather, Otto [8] proposes to commence tanning with a masked chromium salt (2% Cr_2O_3) followed by treatment in chromium oxide solution of twice the initial strength (4% Cr_2O_3) in the form of an entirely cationic salt.

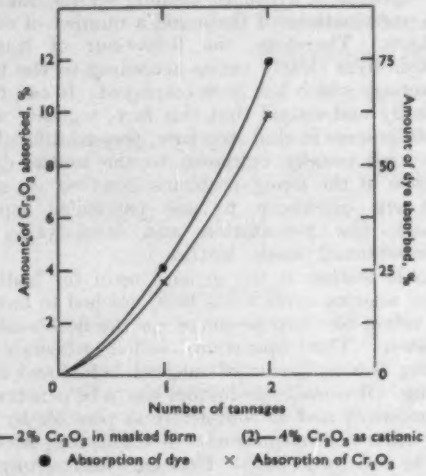

Amount of Cr_2O_3 absorbed, %
Amount of dye absorbed, %
Number of tannages
(1)— 2% Cr_2O_3 in masked form
(2)— 4% Cr_2O_3 as cationic salt
● Absorption of dye
× Absorption of Cr_2O_3

FIG. 3— Effect of tanning with Cr_2O_3 (a) masked, (b) as cationic salt on uptake of Cr_2O_3 and dye (0·03 mol. % Diamine Black BH)

As can be seen from Fig. 3, the uptake of chromium oxide by leather that has been pre-tanned with masked chromium salts is more than doubled, i.e. it is increased to about 10% in the second, purely cationic, tanning operation. The dye fixation is naturally increased correspondingly [9].

Furthermore, the electric charge on suède leather is greatly influenced by other operations, e.g. neutralising, fatliquoring, and drying after tanning. The purpose of neutralising is to suppress the strongly positive charge of the chrome suède so as to ensure that the negatively charged dye ions, as well as the subsequently charged particles of the fat emulsion, are not deposited too rapidly and unevenly on the surface of the leather. Chemicals whose anions have a certain complexing ability are the most suitable for neutralising. They exert a certain reserving action and protect the leather from uneven uptake of dye and fatty compounds on the surface in those areas in which basic chromium compounds have agglomerated during tanning owing to the specific skin structure.

The neutralised suède is dried after a light preliminary fatliquoring to enable it to be wheeled in this state. The chromium complexes are stabilised during the drying process by anionic radicals entering the inner sphere of the complex, thereby impeding the exchange of dye anions.

A preliminary treatment with an anionic fatliquor can also lead to a reduction in the positive surface charge of the chrome suède. For this reason, it is of advantage to use non-ionic or cationic fatliquors for this treatment, since they do not have an unfavourable effect on the charge on the substrate. The distribution and number of the sites in the suède carrying a positive charge can be influenced by correct control of the tanning, neutralising, preliminary fatliquoring, and drying operations with a view to obtaining full and level dyeings.

More uniform penetration and a higher degree of levelling can be achieved by using suitable auxiliaries having affinity for either the fibre or the dye and by bringing about a reversible change in the charge by additions of weak alkalis, e.g. NH_4OH. These additions of auxiliaries or alkalis are made to re-wetting or dyeing liquors. Naturally the success of a dyeing also depends greatly on the selection of appropriate dyes; anionic dyes of moderate penetrating power are the most suitable. Dyes giving superficial dyeings are quite unsuitable, as are dyes that penetrate too deeply into the leather, since they cannot be adequately fixed and may thus tend to bleed out.

The purpose of using small additions of weak alkalis, e.g. ammonia, in re-wetting and dyeing is, firstly, to neutralise the charges on the amino groups of the protein, secondly, to replace the aquo and sulphato groups of the chrome complex with hydroxy ligands, which are less readily displaced by the dye anions, and, thirdly, to retard the formation of dye agglomerates. All these changes reduce the affinity of the dye for the substrate. Once adequate penetration has been achieved they are reversed by using acid (e.g. formic acid), which enables the dye ions to unite with the substrate.

Auxiliaries with affinity for the fibre affect the penetrating and levelling properties of dyes in a somewhat different manner. On account of the structural differences of the skin, it is not possible to obtain completely uniform distribution of the chrome-complex salts throughout the substrate, and the areas having a high chrome content (e.g. the sides) are thus dyed to a fuller depth. Unlevel dyeing of this kind can be prevented by using colourless anionic auxiliaries which, by selective blocking of the positive charges, ensure that the dye exhausts evenly on to the leather. The use of such levelling agents, e.g. a disulphodinaphthylmethane, which has affinity for the substrate, also counteracts too-rapid build-up of dye on the surface of the leather and makes for better penetration.

Apart from the endeavours made to improve the penetration by influencing the strength and uniformity of the surface charge of the leather with auxiliaries having affinity for the substrate, attempts to this end are nowadays increasingly being made by altering the properties of the dyes themselves. The agents employed for this purpose are ethylene oxide condensation products which, by forming a dye–auxiliary agent linkage, alter the exhaustion properties of the dyes and, in some cases, improve their penetrating power. This group of auxiliaries with affinity for dyes comprises condensates of pure ethylene oxide and ethylene oxide with aliphatic compounds, all of which contain reactive groups, e.g. OH, NH_2, COOH. They can be divided into three classes according to their reactivity—

(1) Fatty alcohols having a chain length of 12–20 carbon atoms to which a longer ethylene oxide chain has been added by condensation—

$$CH_3(CH_2)_{11-19}(OCH_2-CH_2)_{13-25}OH$$

(2) Fatty amines having a chain length of 12–20 carbon atoms, each molecule being condensed with two ethylene oxide groups containing 4–20 carbon atoms—

$$CH_3(CH_2)_{11-19}N\begin{matrix}(OCH_2-CH_2)_{4-20}OH\\(OCH_2-CH_2)_{4-20}OH\end{matrix}$$

(3) Fatty alcohols having a chain length of 12–20 carbon atoms condensed with 8–100 ethylene oxide groups, the end-group being sulphated—

$$CH_3(CH_2)_{11-19}(OCH_2-CH_2)_{8-100}OSO_3H$$

The products of class (1) are considered as being non-ionic, even though they have slight cationic character on account of their ether bridges. These compounds have two solubilising groups, the OH group, which reacts independently of temperature, and the ether bridges, whose solubilising action is due to their ability to add water. The addition of water is dependent on temperature, i.e. solutions of the auxiliary products become turbid on heating. The turbidity point lies in the region of 95°C (205°F) and may be lower in the presence of electrolytes. The weakly cationic (so-called "non-ionic") auxiliaries can combine loosely with anionic dyes—

$$D^- + (\text{auxiliary})^+ \rightleftharpoons D\text{–}(\text{auxiliary})$$

The equilibrium in this reaction is in favour of the dissociated products, so that such "non-ionic" compounds do not retard the uptake of anionic dyes. They are mainly used together with dyes that have to be exhausted on to the fibre with an addition of acid, their dispersing action preventing agglomeration of the molecules on the substrate.

The conditions are completely different when dyeing with 1 : 2 metal-complex dyes which are free from sulpho groups. These dyes react with the non-ionic products at the ether bridges—

Thus, a new insoluble group combines with the auxiliary agent. If the dye molecule is large, the dye–auxiliary complex may precipitate to a considerable extent. Conditions when non-ionic products can be used with 1 : 2 metal-complex dyes not containing any sulpho groups are very limited.

The compounds in the second class have three solubilising groups, namely, the temperature-insensitive OH groups, the temperature-sensitive ether bridges, and the basic nitrogen-containing group, which makes the properties of these products dependent on pH. This group of products and the influence they have on the outcome of dyeings produced with anionic dyes of various classes on suède will be discussed in more detail later.

The compounds in the third class again contain ether bridges which are sensitive to temperature, and sulpho groups conferring solubility at all pHs. As the effect of the sulpho group predominates, no turbidity can be observed under normal conditions. These compounds have very little effect when applied in combination with acid dyes, whereas in presence of 1 : 2 metal-complex dyes they have a pronounced retarding and levelling action. The presence of the sulpho group renders the dye–auxiliary complex soluble at all temperatures, and no troublesome side-reactions should thus occur in systems of this kind.

Mode of Action of "Non-ionic" Polyoxyethylene Derivatives in Dyeing of Chrome-tanned Suède Leather

The "non-ionic" polyoxyethylene derivatives of class 2 above have proved to be very suitable as levelling agents in wool dyeing, and they may also be used to improve levelling and penetration of dyes applied to suède leather. We have therefore examined more closely two of the many derivatives belonging to this group. The two products used for our tests were condensation products of long-chain aliphatic amines and ethylene oxide, which are characterised primarily by the length of the ethylene oxide chains attached to the central nitrogen atom. The two chains of the first derivative, Auxiliary A, contain about 10, and those of the second derivative, Auxiliary B, about 30 ethylene oxide units.

Levelling agents of this type possess remarkable properties because of their chemical constitution. The combination of hydrophobic and hydrophilic groups in their molecule not only renders them soluble in water and many organic solvents, but also imparts to them properties typical of surface-active compounds. Their action in the dyeing of suède leather is due mainly to their ability to combine with anionic dyes in acid solutions. As a result the rate of dye uptake is altered, because the reactivity of the dye toward the substrate is lowered.

This reduction in the combining properties which is brought about by addition of auxiliaries having affinity for the dye prevents the dyes from being fixed too rapidly and unevenly on the surface of the leather. Moreover, this decrease in affinity not only improves levelling but in many cases also increases penetration. Auxiliaries A and B can be considered as having affinity for the dye because an acid–base reaction, i.e. a salt formation, takes place between them and the anionic dyes in an acid medium—

$$A + H_3O^+ \rightleftharpoons (AH)^+ + H_2O$$
$$(AH)^+ + Dye^- \rightleftharpoons Dye\ (AH)$$

This salt formation can be assessed by electrometric titration of free dye acid with the relevant bases of the auxiliaries (Fig. 4).

By comparing the titration curves of the dye acid when using either caustic soda or Auxiliary A or B it can be found that one mol base per mol acid is consumed in each case in neutralisation. However, depending on the strength of the base, a dissociation of the salt formed can be observed; as a result the point of equivalence is displaced along the pH axis.

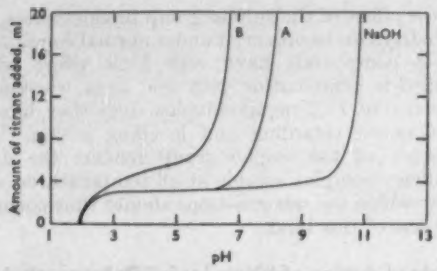


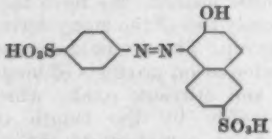
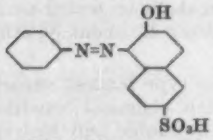
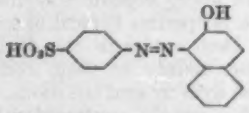
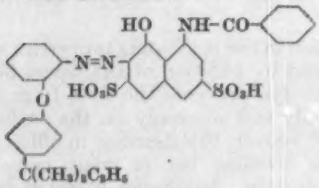
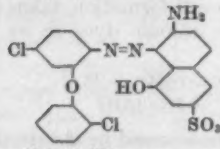
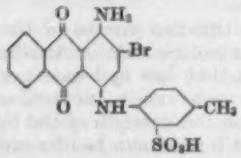
FIG. 4— Titration of free dye acid (Dye VI) with ethylene oxide derivatives and with caustic soda

The changes that take place when additions of Auxiliary A and B are made during the dyeing of suède appear to depend in the first place on the dyeing behaviour of the dye–auxiliary adducts. Since chrome suède leather should not be dyed at a temperature above 65°C (150°F) if it is to be undamaged, dissociation of the dye–auxiliary adducts is reduced to a minimum; this is in direct contrast to the procedure in wool dyeing, where the goods are boiled.

In order to study the behaviour of such dye salts, we carried out a series of tests with six free dye acids of varying constitution and containing

TABLE II

Effect of Auxiliaries A and B on Absorption Curves of Free Dye Acids

Dye No.	Formula	Consumption at point of equivalence of NaOH (100%)	Auxiliary A (100%)	Auxiliary B (100%)	Alterations in absorption curves caused by the addition of Auxiliaries A and B required to reach point of equivalence	λ_{max} (mμ)	A_{max}	[Dye] (%)	$\Delta\lambda_{max}$
I	 Mol. wt. 408 Sulpho group ratio* 204	0·27 g	7·95 g	10·8 g	1 part dye	477·5	0·744	100	—
					1 part dye 7·95 parts Auxiliary A	475	0·457	61·4	−2·5
					1 part dye 10·8 parts Auxiliary B	477·5	0·481	64·7	0
II	 Mol. wt. 328 Sulpho group ratio 328	0·11 g	3·3 g	4·4 g	1 part dye	480	1·172	100	—
					1 part dye 3·3 parts Auxiliary A	475	0·713	60·8	−5
					1 part dye 4·4 parts Auxiliary B	477·5	0·818	69·8	−2·5
III	 Mol. wt. 328 Sulpho group ratio 328	0·10 g	3·4 g	7·6 g	1 part dye	482·5	0·971	100	—
					1 part dye 5·4 parts Auxiliary A	480	0·631	64·9	−2·5
					1 part dye 7·6 parts Auxiliary B	480	0·676	69·6	−2·5
IV	 Mol. wt. 689 Sulpho group ratio 344·5	0·09 g	2·55 g	3·6 g	1 part dye	520	0·600	100	—
					1 part dye 2·55 parts Auxiliary A	525	0·646	107	+5
					1 part dye 3·6 parts Auxiliary B	525	0·661	110·2	+5
V	 Mol. wt. 504 Sulpho group ratio 504	0·07 g	2·25 g	3·0 g	1 part dye	500	0·521	100	—
					1 part dye 2·25 parts Auxiliary A	512·5	0·504	96·7	+12·5
					1 part dye 3·0 parts Auxiliary B	510	0·524	100·6	+10
VI	 Mol. wt. 487 Sulpho group ratio 487	0·07 g	2·25 g	3·2 g	1 part dye	582·5	0·479	100	—
					1 part dye 2·25 parts Auxiliary A	585	0·278	58·0	+2·5
					1 part dye 3·2 parts Auxiliary B	582·5	0·471	98·3	0

*Sulpho group ratio = $\frac{\text{Molecular weight of dye}}{\text{Number of sulpho groups present}}$

different numbers of sulpho groups. These free dye acids were converted quantitatively into "neutral salts" by additions of auxiliaries, the amounts of which were first determined by electrometric titration. A smaller or greater part of the caustic soda or Auxiliary A or B used up at the point of equivalence is spent on neutralising free mineral acids contained in the dyes. As can be seen from the Table II, the first three dye acids are formed from the same parent substance, 1-phenylazo-2-naphthol, and differ only in number and arrangement of the sulpho groups. The same ratio of NaOH : Auxiliary A : Auxiliary B = 1 : 30 : 40 was used in the titration of the three dye acids to reach the point of equivalence.

In a comparison of the dyeing properties of the first three dye acids or of their respective adducts with Auxiliaries A and B, very little difference was observed in dyeings on chrome suède leather. The free dye acids, when applied on their own, penetrate the substrate completely and are fixed to some extent on the fibre, whilst the penetration obtained with adducts is much inferior. The adducts are not fixed and, consequently, can easily be washed off again. The reduction in penetration observed in this case can be explained by Valko's theory [10] that the addition of auxiliaries having affinity for the three dye acids (which are homologues of Orange II) diminishes the diffusion properties of the latter. Such a decrease in the diffusion properties can be traced to the aggregation of the dye–auxiliary salts in the colloidal region, which should affect the absorption spectrum by reducing the optical density. Our measurements clearly confirmed this. All three dye acids have their tinctorial strength considerably reduced by addition of Auxiliary A or B. The stronger and more hydrophobic basic Auxiliary A always reduces the tinctorial strength of the dyes more than does Auxiliary B.

In contrast to the first three dye–auxiliary salts, which are very similar to one another and of simple constitution, the other three dye acids (Table II) form a linkage with Auxiliaries A and B which shows considerably different behaviour both during dyeing of suède leather and in spectrophotometric analysis. Dye acid IV, when applied on its own, does not penetrate the leather but is fixed on the surface. However, a substantial improvement in penetration is obtained if both its sulpho groups are completely blocked by Auxiliary A or B. Auxiliary B produces somewhat fuller depths than the more hydrophobic A. As can be seen from Fig. 5, the absorption curve of the free dye acid IV reaches a maximum at a wavelength of 520 mμ; an abrupt change in direction can be observed at 550 mμ.

Measurements of the two dye solutions containing additions of auxiliary agent showed them to have almost identical spectral curves which, apart from showing a first absorption peak at 525 mμ, also reached a second peak at 560 mμ. In contrast to the previously mentioned dye–auxiliary adducts, their tinctorial strength as determined by means of the extinction coefficients exceeds that of the free dye acid. Auxiliaries A and B bring about a decrease in association of the dye [11], which accounts for the improved penetration obtained.

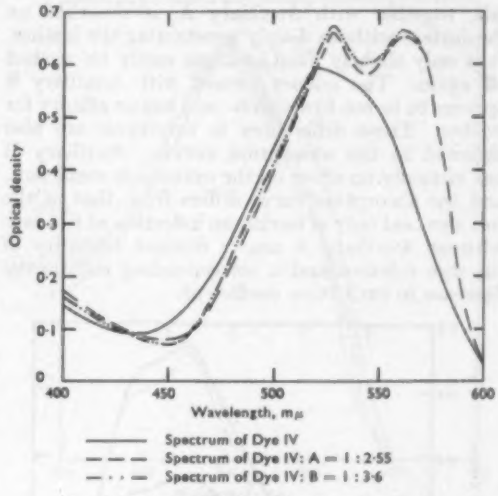


FIG. 5— Effect of addition of Auxiliary A or B on absorption spectrum of Dye IV

Dye V differs in behaviour from Dye IV on account of its much higher sulpho group ratio (ratio of molecular weight to number of sulpho groups). The penetrating power of both the dye acid and the adducts is distinctly lower. By the addition of Auxiliary A or B the absorption curves are moved by 10–12·5 mμ towards longer wavelengths. The curve of the dye–Auxiliary A solution shows a distinct peak at 537·5 mμ. It is possible that a further maximum could be attained by using higher concentrations of Auxiliary A.

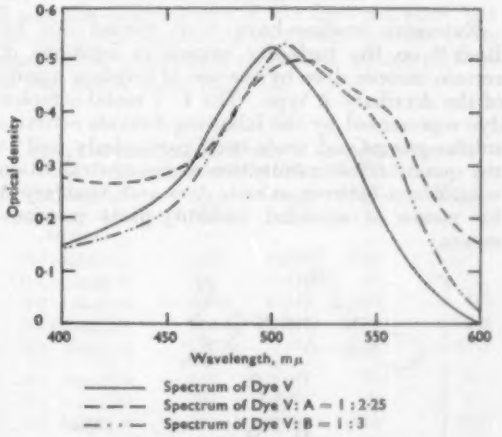


FIG. 6— Effect of addition of Auxiliary A or B on absorption spectrum of Dye V

Since Auxiliaries A and B have only slight effects on the extinction coefficient, the correspondingly slight change in size of the dye aggregates cannot be responsible for the outcome of the dyeings on suède leather. This is mainly due to the more pronounced hydrophobic property of the dye–auxiliary salt as compared with that of the free dye acid, and also to its lower affinity for the substrate.

It is of interest to note the difference in effect which the auxiliaries have on the blue anthraquinonoid Dye VI. In the dyeing process the dye

salt, together with Auxiliary A, is absorbed on the surface without deeply penetrating the leather. It is only slightly fixed and can easily be washed off again. The adduct formed with Auxiliary B appears to be too hydrophilic and has no affinity for leather. These differences in behaviour are also reflected in the absorption curves. Auxiliary B has virtually no effect on the extinction coefficient, and the absorption curve differs from that of the free dye acid only in having an inflection at 615 mμ, whereas Auxiliary A causes distinct turbidity of the dye solution and a corresponding substantial decrease in extinction coefficient.

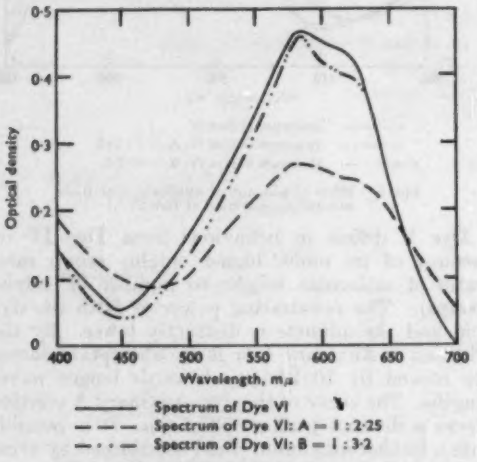
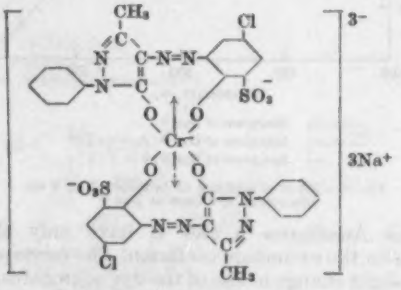


FIG. 7— Effect of addition of Auxiliary A or B on absorption spectrum of Dye VI

Extensive studies have been carried out by Back [12] on the turbidity caused in solutions of certain anionic dyes by the use of levelling agents of the Auxiliary A type. The 1 : 2 metal-complex dye represented by the following formula contains sulpho groups and lends itself particularly well to the quantitative examination of the neutralisation equilibrium between anionic dyes and Auxiliary A by means of so-called turbidity-point measurements.



Molecular weight: 932
Corrected molecular weight: 1170
Number of negative charges: 3

As Back was able to determine, a sodium acetate–acetic acid buffered solution (pH 4·68 at 20°C) of this dye shows considerable turbidity at room temperature when a solution of Auxiliary A is slowly added. By substantially increasing the additions of Auxiliary A the turbidity can be made to disappear completely.

A non-ionic compound with short polyglycol ether chains, e.g. Auxiliary A, shows a characteristic tendency to separate in aqueous solutions under given conditions [13]. When solutions of this kind are heated, colloidal turbidity is observed above a certain temperature; on cooling the turbidity disappears completely. The occurrence of such miscibility gaps can be explained by a decrease in the hydration of the polyglycol ether chains on heating of the solution, whereby the water molecules added to the oxygen atoms of the polyether chains via the hydrogen bridges are split off. These substances are thus less soluble in hot water than in cold. The effect of pH on the tendency to separate has not yet been determined. Naturally, the nature of the components also has an influence. Auxiliary B with its longer polyglycol ether chains is more soluble in water than Auxiliary A, both products having an aliphatic chain of about the same length.

It was of interest to note that the tendency to separate is also evident when a solution of Auxiliary A is added at a constant temperature (80°C; 175°F) to acid solutions of anionic dyes, in particular to solutions of the 1 : 2 chrome-complex Dye M 932 which contains sulpho groups. The temperature at which separation occurs varies with increasing additions of Auxiliary A to a dye solution of constant concentration (Fig. 8).

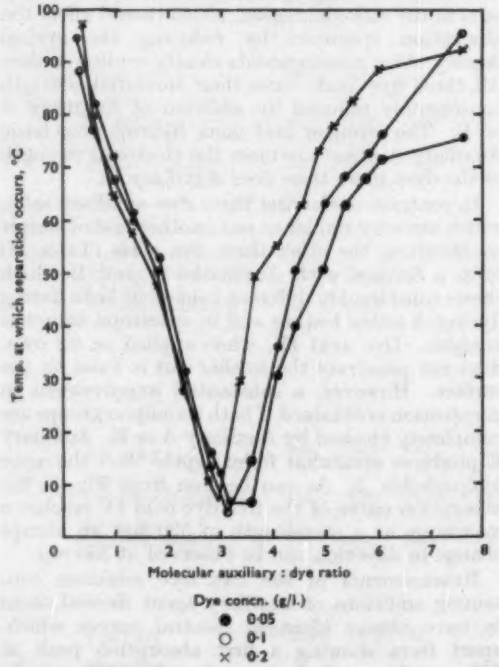


FIG. 8— Miscibility gaps of solutions of chrome-complex dye M 932 in acetic acid–sodium acetate buffer (pH 4·68 at 20°C) in presence of Auxiliary A

At all three concentrations of complex dye M 932 the separation temperature is a minimum at a specific molar ratio which, in accordance with the tribasic nature of the dye, lies at an auxiliary–dye

ratio of 3. This corroborates the assumption made at the beginning that an ion equilibrium exists between the dye anions and the cations of the levelling agent. The neutral salt $D(AH)_3$ in the complex dye–auxiliary combination appears to be sparingly soluble in water. Dispersion of the sparingly soluble salt commences above a molar ratio of 3.

Back carried out similar tests using two other buffer solutions of pH 6·84 and 2·78 under otherwise identical conditions. He then found the temperature minimum of the separation curves to be at lower molar ratios, the more acidic the solutions were. This is further proof of the fact that a dye–auxiliary salt is formed. The lower the pH of the solution the more Auxiliary A is present in cationic form. Because of this the equilibrium of the acid–base reaction is shifted towards the neutral salt. The acid–base equilibrium is composed of three separate steps on account of the tribasic nature of the complex dye—

$$\mathrm{Dye^{3-}} + \mathrm{(AH)^+} \rightleftharpoons \mathrm{Dye(AH)^{2-}}$$
$$\mathrm{Dye(AH)^{2-}} + \mathrm{(AH)^+} \rightleftharpoons \mathrm{Dye(AH)_2^-}$$
$$\mathrm{Dye(AH)_2^-} + \mathrm{(AH)^+} \rightleftharpoons \mathrm{Dye(AH)_3}$$

At the same time it can be assumed that in less acidic solutions the products of the first and second neutralisation steps, which are probably more water-soluble than the "neutral salt" $D(AH)_3$, contribute more to the equilibrium.

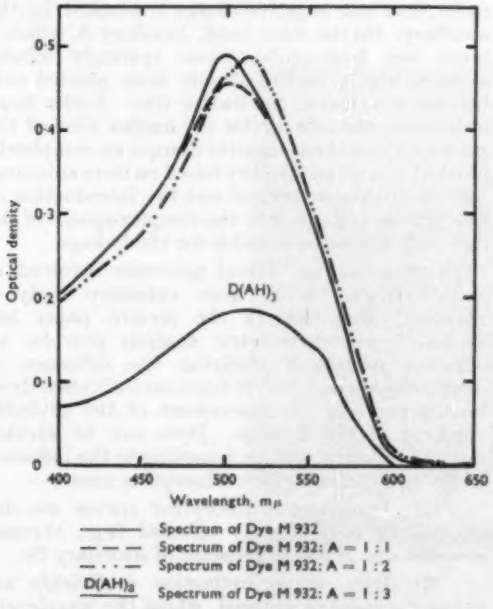


FIG. 9—Effect of molecular ratio of Dye M 932 to Auxiliary A (in acetic acid–sodium acetate buffer at 20°C—pH 4·68) on absorption spectrum of dye

Absorption spectra of solutions with varying dye to Auxiliary A and B ratios confirm Back's results (Fig. 9). For solutions in which the molar ratio of Auxiliary A to chrome-complex dye M 932 is less than 3, the absorption curves differ only insignificantly from those obtained with dye alone in the buffer solution. If, however, only "neutral salt" is present in the solution at an auxiliary:dye ratio of 3, the resulting turbidity (intensive association of the neutral salt in the colloidal region) distinctly lowers the extinction value. (Fig. 10). The absorption spectrum of the solution of the "neutral salt" $D(BH)_3$ formed by Auxiliary B and the complex dye M 932 does not show any change in the extinction coefficient because of its much more hydrophilic properties, as can perhaps be seen better from Table III.

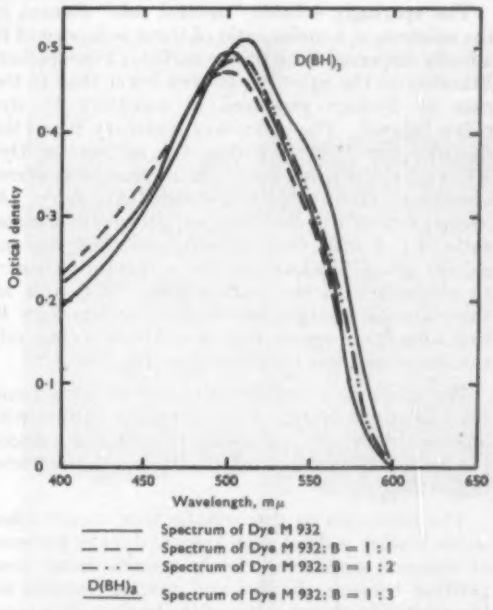


FIG. 10—Effect of molecular ratio of Dye M 932 to Auxiliary B (in acetic acid–sodium acetate buffer at 20°C—pH 4·68) on absorption spectrum of dye

TABLE III

Effect of Auxiliaries A and B on Spectrum of Chrome-complex Dye M 932

Amount of auxiliary agent added*	λ_{max} (mμ)	A_{max}	[Dye] (%)	$\Delta\lambda_{max}$
No addition	500†	0·495†	100	—
0·1 mmol A	500	0·475	96	0
0·2 mmol A	507·5	0·493	100	+ 7·5
0·25 mmol A	512·5	0·507	102	+ 12·5
0·3 mmol A	512·5	0·190	38	+ 12·5
0·1 mmol B	500	0·473	96	0
0·2 mmol B	505	0·491	99	+ 5
0·3 mmol B	512·5	0·508	103	+ 12·5

* Added to 0·117 g dye M 932 in buffered solution at pH 4·68.

† For 0·117 g dye M 932 in unbuffered aqueous solution the respective values are— λ_{max}, 502·5 mμ; A_{max} = 0·497.

Dyeings have been made which show that, as with the dye applied on its own, the adduct in which Auxiliary A and dye M 932 are present at a molar ratio of 1 produces only surface dyeings on chrome suède. In both cases dyeing was carried out in a buffered solution at pH 4·68. However, the adduct was not as well fixed because of the number of dyeing sites that are blocked by the auxiliary agent.

The sparingly soluble "neutral salt" formed in the solution at a molar ratio of three is deposited in a finely dispersed form on the surface of the leather. Fixation on the substrate is even lower than in the case of dyeings produced at auxiliary to dye ratios below 3. The adducts of Auxiliary B and the complex dye M 932 are, like the adducts of Dye VI, distinctly more hydrophilic than the corresponding ones obtained with Auxiliary A, irrespective of whether they are present at a molar ratio of 1, 2 or 3. Only the dye salt which has one sulpho group blocked still has a certain tendency to combine with the leather fibre. If two or all three anionic charges are blocked by Auxiliary B, the adduct separates out of solution as an oily substance and has no affinity for the fibre.

We shall now try to draw some conclusions relating to the dyeing of chrome suède leather with anionic dyes in presence of ethylene oxide condensation products of the type of Auxiliaries A and B.

The reduction in dye uptake that occurs when suède leather is dyed with anionic dyes in presence of anionic auxiliaries clearly results from competition between the dye and auxiliary anions for the positively charged sites of the leather. It is more difficult, however, to explain the levelling action of products such as Auxiliary A and B[14], which have affinity for the dyes. In determining the behaviour of the dye–auxiliary adducts in relation to the dyeing of chrome suède leather, it was necessary to omit a number of ancillary problems. The levelling action of the condensation products A and B in wool dyeing can be considered to be a purely mechanical one. The tendency of the dye–auxiliary adducts to leave the aqueous solution and to attach themselves to the substrate in the form of thin layers leads to uniform coverage of the fibre surface. The layers formed are probably of the mono- or oligo-molecular types. However, it has to be assumed that the dyes containing sulpho groups have practically no affinity for the wool fibre when in the form of their salt-like auxiliary adducts and therefore give completely uniform surface coloration, i.e. all fibres are first uniformly enveloped by this film irrespective of their accessibility and dyeability.

The reduction in affinity may be attributed to the blocking of the sulpho groups in the dye, i.e. dyes containing several sulpho groups blocked by Auxiliary A or B exhibit the same behaviour as dyes which are of similar constitution and which contain no sulpho groups or only one.

On boiling, the dye diffuses uniformly into the wool fibre from the thin film formed on the surface. During diffusion into the interior of the fibre a dissociation of the "neutral salt", first to the lower neutralisation steps and then to the dye anion and auxiliary cation, takes place. The dyes containing sulpho groups are then fixed primarily to the amino groups of the wool by a salt-like linkage, whilst the fixation of the auxiliary cations by the hydroxyl groups of the wool may be incomplete. According to the theory that the dye–auxiliary adducts produce a thin film on the surface of the fibre, the amount of Auxiliary A or B required depends not only on the concentration of dye used but also on the surface area available on the fibres to be dyed.

The dissociation of the "neutral salts" to the lower neutralisation steps and dye anions and auxiliary cations when wool is dyed can take place only gradually or not at all in the dyeing of chrome suède leather, on account of the low dyeing temperature employed. Therefore, the affinity and solubility of the salt-like adducts composed of dyes containing sulpho groups and levelling agents of the Auxiliary A or B type are of greater importance than in wool dyeing. These properties can, to a certain extent, be associated with the "sulpho group ratio" of the dyes (ratio of the molecular weight of the dye to the number of sulpho groups present). It is important to note that the higher the sulpho group ratio and the more hydrophobic the levelling agent used, the less soluble are the dye–auxiliary salts in water. On the other hand, with a lower sulpho group ratio, the corresponding salt-like addition compounds become more hydrophilic. Dyes of high sulpho group ratio form sparingly water-soluble salt-like adducts even with the hydrophilic Auxiliary B.

For example, Auxiliary B forms highly hydrophilic adducts with the complex dye M 932 which show only a slight tendency to colour leather. A certain degree of affinity is found only when not more than one negative charge is blocked by the auxiliary. On the other hand, Auxiliary A, which is much less hydrophilic, forms sparingly soluble adducts which, as has already been pointed out, become attached to the leather fibre. Under these conditions, the affinity for the leather fibre of the product whose three negative charges are completely blocked is in all probability based on mere adhesion, but the hydrogen bridges and the introduction of free protein radicals into the complex sphere of the dye may also be responsible for the linkage.

To elucidate the actual processes involved in leather dyeing much more extensive study is required. However, as the present paper has shown, spectrophotometric analysis provides an effective means of studying the influence of auxiliaries of the A and B types on individual dyes, thus permitting the assessment of the probable outcome of the dyeings. Dyes can be divided into the following groups according to the influence of the auxiliaries on their absorption curves—

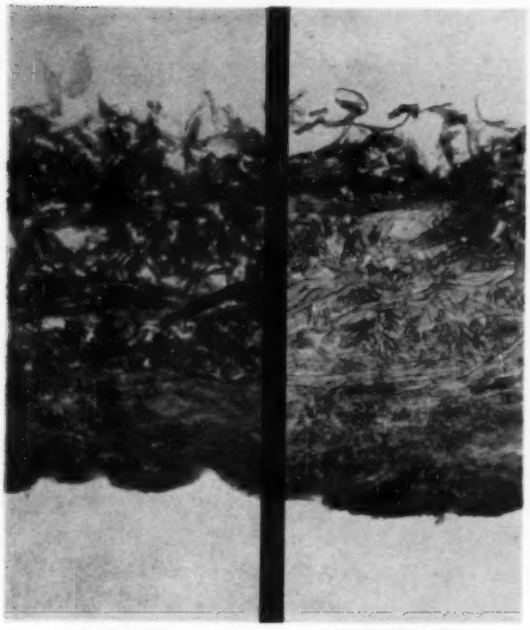
(1) Dyes whose absorption curves are unaffected or only slightly affected (e.g., chrome-complex dye M 932 in presence of Auxiliary B)

(2) Dyes whose extinction coefficients are either increased or lowered, whilst the wavelength of maximum absorption is only slightly affected (e.g., Dyes I–III)

(3) Dyes whose extinction coefficients are either increased or lowered, whilst the wavelength of maximum absorption is distinctly affected (e.g. Dye V)

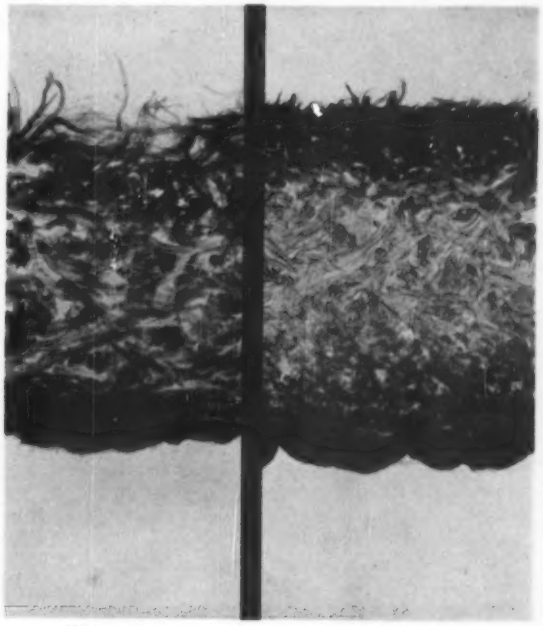
(4) Dyes whose spectra show an additional absorption peak as well as an increase or decrease in extinction coefficient (e.g. Dye IV).

Effect of Auxiliary B on penetration of dyes into leather



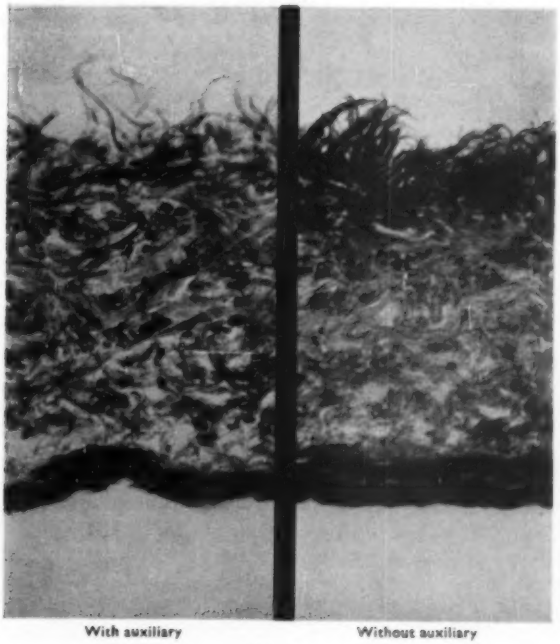
With auxiliary Without auxiliary

FIG. 11



With auxiliary Without auxiliary

FIG. 12



With auxiliary Without auxiliary

FIG. 13

To carry out a successful dyeing on chrome suède leather the dyes should be selected according to the following principles—

(1) The affinities of the individual dyes for chrome suède leather should not differ greatly.

(2) The additions of auxiliary agents should minimise differences in affinity of the dyes by forming adducts.

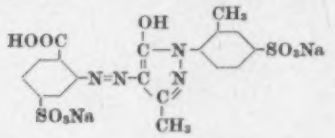
(3) The absorption spectra of the dyes selected should show similar changes on addition of the auxiliaries.

The influence of these auxiliary agents on the outcome of dyeings on leather is clearly visible in the micrographs, which show cross-sectional cuttings of chrome-tanned suède leather dyed with and without the aid of Auxiliary B. In Fig. 11 the dye acid alone exhibits little tendency to penetrate, whereas with Auxiliary B penetration is practically complete. This illustrates very clearly the extent to which an auxiliary agent is able to influence the properties of a given dye. The absorption curves of the two solutions are very little different, so that in this case it is mainly the affinity of the dye which has been reduced by blocking the negatively charged sulpho groups.

The selective influence upon certain dyes is perhaps more apparent in Fig. 12, which consists of micrographs of dyeings made by means of a yellow, a red, and a blue chrome-complex dye.

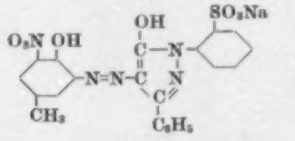
The use of Auxiliary A or B has been found to be particularly advantageous when producing trichromatic dyeings on chrome suède leather by means of a yellow, a red, and a blue dye. Of the many dyes tested, the following three 1 : 1 chrome-complex dyes in particular have proved to be suitable:

(*a*) yellow 1 : 1 chrome-complex of—



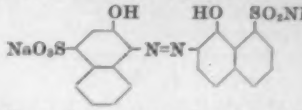
C.I. 19010

(*b*) red 1 : 1 chrome-complex of—



C.I. 19115

(*c*) blue 1 : 1 chrome-complex of—



C.I. 15050

The yellow chrome-complex dye exhibits somewhat less affinity for chrome leather than the other two components. Thus the yellow dye completely penetrates the leather, whereas the red and the blue dyes build up on the surface only. A dyeing of this kind is naturally highly unsuitable in view of the subsequent buffing of the leather, since the dyes are not uniformly distributed throughout the cross-section of the leather. However, the differences in affinity of the three chrome-complex dyes are such that suitable additions of Auxiliary A or B are capable of balancing them up by forming adducts. By comparing the dyeings produced with and without additions of auxiliaries, it is seen that the cross-section of the leather is dyed uniformly in the presence of an auxiliary, whereas this is not so when no auxiliary is employed.

Fig. 13 shows a similar dyeing with the same components. In absence of auxiliary agent, the blue dye remains in the surface areas of the leather, but is dispersed well into the interior regions of the interwoven fibre structure with the aid of Auxiliary B.

These dyeings clearly show the great advantages which the use of levelling agents of the Auxiliary A and B type has to offer, especially where differences in penetration and affinity of the dyes used would normally present difficulties.

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References

[1] McLaughlin and Theis, *Chemistry of Leather Manufacture*, p. 12 (1945).
[2] Stubbings, *J. Amer. Leather Chem. Assocn.*, **51**, 545 (1956).
[3] Cassel and Kanogy, *ibid.*, **44**, 424, 442 (1949).
[4] Otto, *Das Leder*, **1**, 81, 105, 133 (1950).
[5] Küntzel, *Angew. Chemie*, 307 (1937).
[6] Elöd and Hänsel, *Collegium*, 763 (1933).
[7] Mauthe and Faber, *Das Leder*, **4**, 50 (1953).
[8] Otto, *ibid.*, **2**, 1 (1951).
[9] Idem, *ibid.*, **2**, 3 (1951).
[10] Valko, *J.S.D.C.*, **55**, 173 (1939).
[11] Luck, *Angew. Chemie*, **72**, 63 (1960).
[12] Back, unpublished work.
[13] Luck, *Farbenchem. Kolloquium*, Basle Univ., 27th Jan. 1959.
[14] Luck, *Angew. Chemie*, **72**, 57 (1960).

Discussion

Mr. H. R. HADFIELD: What do the authors consider to be the relation between a change in absorption spectrum and the dyeing properties of a dye–agent complex? It is suggested that a reduction in absorption maximum, corresponding to the formation of a dye–agent complex, results in a significant reduction of the dyeing rate, yet Casty has published information to show that on wool the formation of complexes actually increases the dyeing rate. How can these two views be reconciled?

Have the authors attempted to correlate the formation of complexes with the properties of the dye? They would, perhaps, be interested in a paper published this year in the *Journal* by Craven and Datyner, where a correlation between complex formation and the hydrophobic properties of the dye is established.

Dr. HERNDL: According to R. Casty (*SVF Fachorgan*, **13**, 486 (1958)), the addition compounds formed under acid conditions between ethylene oxide condensation products of group 2 (p. 649) and

certain anionic dyes are taken up fairly rapidly by the wool fibre at a relatively low temperature (60°C). As examinations have shown, the dye–auxiliary product at first forms only a uniform sheath-like coating over the surface of the wool substrate. It is only at a higher temperature that the dye is capable of penetrating from this coating into the interior of the fibre.

The acceleration by the auxiliary agent of the uptake of dye, as pointed out by Casty, applies only to the first stage of the dyeing process. The second stage, in which cleavage of the adduct and penetration of free dye into the fibre take place, does not always proceed rapidly.

As has been mentioned by Craven and Datyner (J.S.D.C., **77**, 304 (1961)), no direct relation exists between the rate of uptake and the alteration in the absorption of dye solutions caused by the influence of auxiliaries with affinity for the fibre. However, these authors point out that it is primarily the force with which the dye–auxiliary adduct is held together that has a decisive influence on the yield of wool dyeings.

If a substrate, e.g. suède chrome calf leather, has to be dyed at a lower temperature, it is very likely that the dyeing behaviour of the dye–auxiliary adduct is mainly responsible for the yield. With the majority of these adducts, cleavage can be expected to take place only at a fairly high temperature.

The following brief statement can be made on the relation between changes in absorption spectra and dyeing behaviour:

A lowering in the optical density of the dye solution brought about by the addition of auxiliaries points to an increase in aggregation. On the other hand, a highly aggregated compound penetrates the leather much more slowly than the free dye in a state of lower aggregation. This can only be explained by the fact that the dye–auxiliary aggregates have to overcome greater diffusion forces which are not encountered in the first phase in wool dyeing. It is therefore very likely that even large dye–auxiliary aggregates are taken up by the wool more rapidly than the free dye. A reduction in extinction is therefore usually evident in leather dyeing by a retardation in dye uptake, which is not necessarily the case in the dyeing of wool.

Mr. R. K. FOURNESS: The points on the lower curve of Fig. 2 imply that measurements of the Cr_2O_3 absorbed were made after $\frac{3}{4}$, $1\frac{1}{2}$, $2\frac{1}{4}$, $2\frac{3}{4}$, and so on, tannages had been performed. What is the true meaning of this?

Dr. HERNDL: The points on the lower curve of Fig. 2 do not correspond with the actual experimental values, but simply indicate this curve as the one pertaining to the absorption of Cr_2O_3. Naturally, the measurements were made after completing each individual tanning operation.

THURSDAY MORNING, 21st SEPTEMBER 1961

Chairman— Mr. C. PAINE

Modern Physical Techniques in Colour Formulation

J. V. ALDERSON, E. ATHERTON, and A. N. DERBYSHIRE

The possibilities of using modern physical instruments in colour control and formulation are discussed, with specific reference to filter colorimeters, spectrophotometers, and high-speed electronic digital computers. It is shown that visual assessments can be used to calibrate colorimeters, so that measurements of small colour differences may be expressed in colourist's terminology. An electronic computer has been programmed, to enable rapid colour-matching calculations to be carried out. The applications and implications of this method are discussed.

Introduction

Colour, as it concerns the dye and pigment technologist, is a subject shorn of its poetic aspect. The colourist rarely indulges, because of lack of either inclination or opportunity, in those flights of fancy to which his artistic and scientific counterparts in the fields of applied colour are prone, but his particular use of colour calls for as much judgment as does theirs. His skills are not to be acquired without considerable labour and application, and it is therefore not surprising if he views with reserve attempts to reduce some of his activities to exercises with physical instruments. The fact is that the average colour technologist is a shrewd and thoughtful individual who must be prepared on occasions to back his judgment of colour and its formulation when large sums of money are at stake. The successful colourist is the one who guesses correctly more often than not, and who possesses sufficient skill or personality to cope with his partial failures without loss of prestige.

At present, a minor revolution is in inception in the colour-using industries. The physicist is now able to provide optical instruments which are capable of recording colour in numbers, to limits of precision comparable with the smallest differences that can be seen by eye. The interpretation of these numbers in terms familiar to the colourist can be made, although there is no unique translation that can be invoked in instrumental applications because of differences in colourist's terminology and in criteria applied in different industries. The task of relating the readings of any particular colorimeter to colourist's terminology is probably better undertaken by the colourist with a basic knowledge of colour physics than by the professional physicist. Certainly the necessary knowledge can be acquired more easily by the former than can the formidable technology of colour application be absorbed by the latter.

In this respect the full exploitation of current instrumental development must depend in the first instance upon goodwill and application by colour users. This does not imply that the uncritical use of any physical instrument on complicated problems will be attended by success. Instruments must be applied at first with caution until, assuming a suitable instrument is employed, it is possible to delegate certain phases of colouring processes to routine instrumental analysis. The ultimate goal of completely instrumental colour technology has not yet been achieved, but it would be unwise to deny the possibility of this in the next few decades. Short of this, at present, utopian solution, it is clear that already colorimeters are being purchased by the colour-making and colour-using industries in increasing numbers, and are proving advantageous from economic and quality standpoints. The present paper is an attempt to review some of the recent practical applications of physical instruments to the fields in which the colourist operates, to assess the part they can play in different phases of practical operation, and to indicate likely future trends.

Subjective Colour Estimation and the Formulation of Colorant Mixtures

Many of the problems confronting the colourist are concerned with the selection and formulation of dye or pigment mixtures to produce a colour matched to a specified sample and to judge by eye the magnitudes and significances of colour differences between dyed or pigmented patterns.

In order to describe a colour difference in significant terms, the colourist must use variables that can be conveniently adjusted in practice. There would be, for example, little point in describing the difference between two patterns as one of lightness, since no single practical adjustment (e.g. addition of more of an existing dye in a mixture or introduction of dye of a different hue or a brighter dye of the same hue) will remove a difference of lightness. A much more significant description is obtained in terms such as strength, since changes of colour produced when more or less of a dye is used are, by definition, changes of strength.

The colourist is able not only to describe colour differences in terms such as strength, but also to estimate quantitatively the magnitudes of these differences. This skill is learned only by experience and with careful tutelage, and forms the traditional basis for colour assessment in the colour-making and colour-using industries.

It would be idle to pretend that even an experienced colourist is perfectly reproducible in his judgments, compared either with his own past

assessments or with the assessments of other, equally skilled, colourists. This must be true, because the standards of colour-matching demanded are pushed increasingly towards the limit of perception. The colourist has perceptive equipment which is basically no better than that of the man who may complain about the results of his work. To complain it is only necessary to perceive a difference of colour, but the colourist must perceive, assess, and often correct a colour difference. Thus, from a functional viewpoint, a colour difference exists for the colourist only if he can not only perceive it, but also describe it unambiguously in terms of its attributes (strength, shade, and brightness). In this situation he is at a disadvantage because he must work with increments of colour that are only just within his powers of discrimination, and is therefore not completely reproducible in judgment.

In the practice of his skill he is also conscious of other, non-technical, factors which are often mutually incompatible, e.g. the need for speed so as to avoid losses from idle capital equipment or stock and the even greater loss that might be involved in a snap judgment, if a justifiable complaint were to arise subsequently.

The way in which these requirements on performance are met by different individuals leads to different interpretations of the concept of a significant colour difference. If it is taken that such a difference, related to any one of the three attributes strength, shade, and brightness, is the smallest that can be perceived with certainty by a colourist, and is called a trace, the following data illustrate the variations which occur. They are drawn from a survey carried out by McLaren[1], the assessments all having been made by colourists of over five years' experience. Large numbers of pairs of patterns covering a wide range of hues were prepared, showing small non-metameric differences in shade and brightness, but not in strength. These were assessed by the colourists, and the mean assessment for each pair and the frequency of individual deviations from it were determined. Departures of individual assessments from the mean were then as shown in Table I, in which all the results have been combined since there is no significant difference in accuracy when judging shade or brightness.

TABLE I

Difference from mean assessment (Traces)	Individual assessments (%)
−2	3
−1	24
0	50
+1	20
+2	3

This distribution is approximately Gaussian in form and corresponds to a standard deviation of about one trace. Thus, although the individual colourist thinks of a trace as the smallest difference in any attribute of colour that he can perceive with certainty, it appears that the trace represents his standard deviation from the group judgment—i.e., the individual will differ by more than a trace from the group judgment once in every three assessments.

THE INSTRUMENTAL APPROACH TO COLOUR

The basic philosophy of the instrumental approach is to establish techniques, associated with physical instruments, that will enable the colour perception of the normal individual to be expressed quantitatively and thus to provide a universally acceptable reference system for use in scientific and commercial applications of colour.

Colour, as it concerns the dyeing and pigmentation industries, is produced by a process of selective absorption of light. Clearly, the factors that can influence colour are the distribution of energy in the illumination under which the colour is perceived, the way in which the dye or pigment modifies this distribution, and the translation of this modified light into colour by the normal eye. The first two factors are amenable to exact physical specification, but the colour-translating properties of the eye are more obscure. Although many physiological studies [2] have been carried out into the stimulation of the eye by light, it is clear that simple specification is necessary for the establishment of a practically convenient system of instrumental colour specification. A suitable basis was provided by Wright [3] and by Guild [4], who used the principle of equivalent stimuli in experiments in which the individual wavelengths of the visual spectrum were colour-matched by normal observers, using adjustable amounts of three physically defined light sources or primaries, coloured red, green, and blue.

The data of Wright and Guild were adopted by the CIE (Commission International d'Eclairage) in 1931 [5], as defining the colour perception of the normal eye in terms of three defined standards. The way was now clear for the full practical exploitation of instrumental colorimetry. For a variety of reasons, however, progress was slow. The necessary instrumentation included a spectrophotometer, to determine the light-reflecting or -transmitting properties of the material whose colour was to be specified and, in view of the large number of colour determinations necessary in any practical application, a costly recording spectrophotometer was desirable. This virtually restricted use of the technique to large companies and academic institutions, particularly in the U.S.A., where a recording spectrophotometer (the G.E. instrument) [6] was available from the late 1930s. In 1949, a further boost was given by the introduction of the Librascope tristimulus integrator [7], by which the tristimulus values—

$$\left.\begin{aligned} X &= \int E_\lambda . R_\lambda . \bar{x}_\lambda . \mathrm{d}\lambda \\ Y &= \int E_\lambda . R_\lambda . \bar{y}_\lambda . \mathrm{d}\lambda \\ Z &= \int E_\lambda . R_\lambda . \bar{z}_\lambda . \mathrm{d}\lambda \end{aligned}\right\} \quad \ldots . (1)$$

were computed automatically while the spectrophotometric curve was being drawn by the G.E. Spectrophotometer.

The integrator–spectrophotometer combination was shown by Davidson and Imm [7] to be capable of discriminating colour differences corresponding to about one trace [8]. A breakthrough had been achieved that made possible practical instrumental colorimetry but at a cost (approximately £10,000) that was beyond the means of many potential users.

The next significant advance was the appearance of the Hunter Filter Colorimeter [9], which enabled values of X, Y, and Z to be determined by measuring a sample with a lamp–filter–photocell combination so chosen that the weighting factors E_λ and $\bar{x}_\lambda$, $\bar{y}_\lambda$, $\bar{z}_\lambda$ in Eqn. 1 were multiplied by the reflectance R_λ and the integrals derived automatically. This method brought about a spectacular reduction in the cost of the equipment for practical colorimetry, and in the ensuing years many instruments based on the same principle have been marketed.

The absolute accuracy of this type of instrument is limited essentially by the extent to which the characteristics of the lamp–filter–photocell combination used reproduce the CIE Standard Observer Data, and in most commercial instruments significant deviations are found. The importance of these deviations will depend very much on the use which is made of the instrument. They will clearly limit the accuracy of measurement of a single pattern, so that the tristimulus values obtained must be regarded as only an approximate indication of the absolute values. Their importance in the measurement of colour difference will depend on the degree of metamerism between the patterns being compared. For non-metameric or only slightly metameric combinations, exact reproduction of the Standard Observer Data is not important, and instrumental results can be shown to correlate excellently with visual assessments (discussed in detail in the next section). Consequently, this type of instrument can be used for standardisation of known colorant mixtures, and also for match prediction if precautions are taken against using recipes showing large metameric differences.

In measurement of metameric pairs, instrumental deviations from the Standard Observer Data will clearly give results that do not correlate with visual assessment of colour differences. In this situation, however, the more exact procedure of integrating reflectance curves measured on a spectrophotometer may still not produce instrumental values in complete accord with visual assessment. This is not surprising, for quite marked variations in assessment of metameric differences are found from one observer to another, owing to slight differences in colour vision and macular pigmentation, and this must obviously limit the agreement which can ever be obtained with instrumental values. There is, furthermore, a limitation imposed on the CIE data themselves which may be of importance in the measurement of metameric pairs. The Standard Observer Data are based on measurements in a 2° field of view, which is much smaller than the one commonly employed in colour-matching work. Consequently, it is possible for completely accurate CIE tristimulus values for metameric pairs still to show systematic differences from average visual assessment, because of this difference in viewing conditions. Recently, data have been published for a 10° field [10], although these results have not yet been officially adopted by the CIE. It may well be that use of these new results in place of the original Standard Observer Data will improve agreement between instrumental and visual assessment of metameric differences. In the meantime it must be concluded that application of photoelectric colorimeters is best confined to patterns showing only slight metameric differences. This principle has been applied to all of the work described in this paper: strongly metameric matching has been avoided and use of absolute colour measurement has been confined to formulation of first-trial dyeing recipes, where the inevitable inaccuracy of the absolute values can be corrected by subsequent adjustments to the recipe.

The instruments used in this work are the G.E. Recording Spectrophotometer [6] and the Colormaster Differential Colorimeter [11], both of which are adequately described in the literature. The spectrophotometer was used for the measurement of complete reflectance curves, to establish the adequacy of the equations used in the methods of match prediction described, and to derive the necessary data on individual dyes for the practical application of such methods. The Colormaster was used to establish the relations between instrumental and visual assessments of colour difference, and also for the measurement of patterns in the investigation of instrumental colour matching.

Applications of Physical Methods

THE RELATION OF COLOURIST'S TERMINOLOGY TO COLORIMETER VARIABLES

Instrumental colour measurements are normally expressed in the first instance as the X, Y, and Z tristimulus values of the CIE system, of which the value Y has the special significance of representing the luminance of the material. To assess the significance of these values it is convenient to form from them two other variables, the chromaticity coefficients, defined by—

$$\left.\begin{aligned} x &= X/(X+Y+Z) \\ y &= Y/(X+Y+Z) \end{aligned}\right\} \quad \ldots\ (2)$$

The chromaticity coefficients between them represent the attributes of hue and purity, and together with the luminance value Y again provide a unique specification of the colour. The chromaticity coefficients may be plotted in a plane figure (Fig. 1) to produce the chromaticity diagram, in which the white point is towards the centre of the figure and the spectrum locus together with the line joining the ends of the locus define the limits of physically realisable colours, so that all real colours must plot within this area. Then the hue of a colour is indicated approximately by the hue of the spectral colour to which a line from the white point through the x, y values of the colour projects (the dominant wavelength), and its purity is indicated by relative

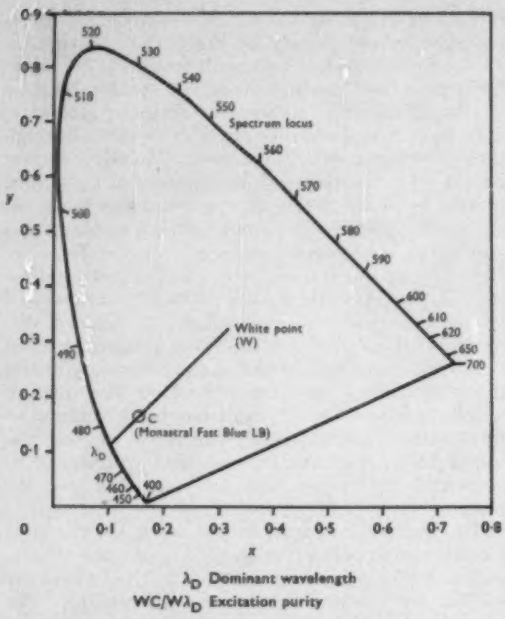

FIG. 1— Dominant wavelength and excitation purity of Monastral Fast Blue LB

distance along this line towards the spectrum locus.

It is apparent that, when chromaticity differences are expressed in this way, physical meaning can readily be attached to them, and also to differences in lightness, but these differences will still not correlate directly with the colourist's terminology. A further serious drawback to this system as it stands is that a given numerical change in chromaticity in various regions of the chromaticity diagram by no means represents an equal visual change of colour. Similarly, a given numerical change in luminance does not represent an equally apparent lightness change at different lightness levels. Numerous attempts have been made to correct for this by transforming the chromaticity co-ordinates and the luminance values to new variables, in which a given change in any of the variables will be equally apparent visually at all points of colour space, but none of these can be claimed to be completely successful. By combining the transformed variables into a single equation, any colour difference can be expressed as a single scale which should indicate numerically its apparent magnitude. The N.B.S. unit of colour difference [12] has been derived in this way, and while its use in industrial applications in the U.S.A. appears to be fairly widespread, it is not extensively used in this country.

Another method of defining a system of equal colour spacing is to develop a series of permanently coloured chips having equal apparent differences from one chip to the next. One of the best known of these is the Munsell system [13], where the chips form a cylindrical array in which the central axis consists of a set of equally visually spaced neutrals from black to white. The distance along this axis represents the Munsell value of the neutrals and also of colours lying on the same plane but away from the neutral axis by a distance representing the Munsell chroma. The Munsell hue circle is represented by angular movement around the cylinder. The spacing of patterns on this system is generally accepted as being visually satisfactory, and the colour co-ordinates of these patterns have been used to develop and check the uniform chromaticity systems referred to above. It will be noted, however, that the Munsell system still effectively retains a function of luminance only as one of its variables, so that it would be anticipated again that differences expressed in this system will not correlate directly with the colourist's variables.

The alternative to any of these approaches is to translate directly from instrumental measurements of colour difference into the language of the colourist. This can be done in any particular small region of colour space by direct correlation experiments in which pairs of patterns are measured on an instrument and also assessed by colourists. It has the great advantage that the precision of the instrumental approach is expressed directly in terms that the colourist can appreciate, and so the utility of the method for practical applications can readily be assessed.

The Transformation Equations

Since either of the two sets of variables, x, y, Y, and strength, shade, brightness, can be used to specify any colour uniquely, it is clear that any variable of the one set may be regarded as a function of the three variables of the other set. For example, strength may be regarded as some function of x, y, and Y. If the calculus of small variations is applied to this function, it is possible to write a small variation in strength ΔS in terms of the three partial differentials, as shown in Eqn. 3—

$$\Delta S = \left(\frac{\partial S}{\partial x}\right).\Delta x + \left(\frac{\partial S}{\partial y}\right).\Delta y + \left(\frac{\partial S}{\partial Y}\right).\Delta Y \quad \ldots . \quad (3)$$

where S is the strength as a function of x, y, and Y, and Δx, Δy, ΔY is the instrumental colour difference corresponding to a visual difference of ΔS traces of strength. The values of the three differentials in Eqn. 3 will depend on the colour about which the variation is being made, but for a given colour (the colour of the standard product in the case of colour standardisation) these will have a constant, but as yet unknown, value. Using an identical analysis for the remaining two visual variables, Eqn. 4 are obtained—

$$\left.\begin{aligned} \Delta S &= (a_1\times\Delta x) + (b_1\times\Delta y) + (c_1\times\Delta Y) \quad \text{for strength} \\ \Delta G &= (a_2\times\Delta x) + (b_2\times\Delta y) + (c_2\times\Delta Y) \quad \text{for shade (greenness)} \\ \Delta B &= (a_3\times\Delta x) + (b_3\times\Delta y) + (c_3\times\Delta Y) \quad \text{for brightness} \end{aligned}\right\} \ldots . \quad (4)$$

It should be noted that Eqn. 3 is accurate only for very small colour differences, as terms of second and higher order have been ignored. It has, however, been found that linear equations represent the situation sufficiently well for the size of colour difference experienced in practical standardisation to justify the neglect of these terms.

Once the nine constants of Eqn. 4 have been determined for a particular standard colour, it will clearly be easy to use the equations to calculate the colour difference in traces from the instrumental difference Δx, Δy, ΔY. The standard colour chosen for the first experiment was a saturated blue, the blue used in practice for the standardisation of the paint pigment Monastral Fast Blue LB (C.I. Pigment Blue 15). The reason for choosing a blue was that, in the blue region of the chromaticity diagram, published data [14] indicate that the eye is most sensitive to a given chromaticity difference, and therefore by choosing to operate in this region the sensitivity of the colorimeter was most searchingly tested. Coloured paint films rather than textile substrates were chosen because of the possibility of preparing smooth uniform patterns and thus ensuring that real colour differences rather than differences in surface structure were being measured and assessed.

As the nine constants of Eqn. 4 have to be determined statistically, a large number of patterns showing small colour differences from the standard had to be prepared, and a number of assessors had to be used. The standard paint was made up and fifty patterns of painted card were made from this standard paint shaded to various extents with small amounts of shading paints. Three series of patterns were made, one by shading the standard paint with white to produce a series with strength variations, one by shading with green and violet paints to produce a series with mainly shade variations, and one by shading mainly with a grey paint to produce a series with brightness variations. All these patterns were assessed against the standard colour by thirteen assessors in terms of strength, shade, and brightness, and the means of the assessors' results were formed. The patterns were also measured on the Colormaster Differential Colorimeter and the colour differences from the standard recorded as Δx, Δy, ΔY. The nine constants of Eqn. 4 are obtained from these data by the method of least squares, to give the following equations—

$$\left.\begin{aligned} S &= 1165\,\Delta x + 217\,\Delta y - 3{\cdot}80\,\Delta Y \quad \text{for strength} \\ G &= 1196\,\Delta x + 402\,\Delta y + 0{\cdot}72\,\Delta Y \quad \text{for greenness} \\ B &= 431\,\Delta x - 254\,\Delta y + 2{\cdot}31\,\Delta Y \quad \text{for brightness} \end{aligned}\right\} \quad \ldots\ldots (5)$$

Negative signs arising from the use of Eqn. 5 indicate the presence of weakness, redness, or dullness, respectively.

Eqn. 5 represent the way in which variations in chromaticity and luminance about a certain blue standard are connected with the corresponding mean visual appearance to the eyes of thirteen trained assessors. The validity of Eqn. 5 may be seen from the fact that the correlation coefficient between the assessors' mean results and the assessments calculated using the equations is 0·95. As the colour differences used in the derivation of the equations were mainly of one attribute only, and as they had been artificially produced by shading with other coloured paints, it was thought desirable to check the validity of the equations for colour differences in cases where all three attributes were varying together and where the colour differences were of a natural origin (variation of crystalline form or particle size). Table II shows

TABLE II

Comparison of Instrumental and Colourist Assessment of Colour Differences

Sample	Strength Assessment		Shade Assessment		Brightness Assessment	
	Mean colourists' assessment	Colormaster assessment (Traces)	Mean colourists' assessment	Colormaster assessment (Traces)	Mean colourists' assessment	Colormaster assessment (Traces)
1	3 traces weaker	−4·4	Equal	−0·7	2 traces duller	−2·2
2	2 traces weaker	−3·0	Equal	−0·2	2 traces duller	−2·5
3	Equal	−0·9	1 trace redder	−1·6	3 traces duller	−2·2
4	Equal	+0·4	Equal	−0·8	3 traces duller	−2·6
5	3 traces stronger	+3·7	2 traces redder	−1·9	3 traces brighter	+4·0
6	2 traces weaker	−1·4	Equal	+0·3	1 trace duller	−1·8
7	1 trace stronger	+0·9	1 trace redder	−2·0	2 traces brighter	+2·3
8	2 traces weaker	−1·8	1 trace redder	−0·3	2 traces duller	−0·9
9	Equal	+0·2	Equal	+0·1	3 traces duller	−3·4
10	3 traces stronger	+3·3	1 trace redder	−1·5	3 traces brighter	+2·3
11	Equal	+0·2	1 trace greener	+1·0	1 trace duller	−1·4
12	3 traces stronger	+3·8	1 trace redder	−2·4	3 traces brighter	+3·7
13	1 trace stronger	+2·7	Equal	−0·5	3 traces brighter	+2·6
14	1 trace stronger	+2·2	1 trace redder	−1·2	2 traces brighter	+2·6

that there is good agreement between the visual assessments and the values calculated from Eqn. 5 in these cases.

A Geometrical Interpretation of the Transformation Equations

The derivation of equations relating the visual system to the instrumental system of colour difference measurement has so far been treated as an exercise in the statistics of finite differences. There is, however, another way of looking at the formation of the equations which perhaps gives a clearer picture of their physical meaning. The chromaticity diagram, together with the third dimension of luminance, can be regarded as an ordinary three-dimensional volume, a colour space, in which every point represents a different colour, with adjacent colours merging imperceptibly into their neighbours. At one particular point in this colour space lies the saturated blue colour that has been chosen as the standard colour for this work. From this point, movements can be made in any direction, but there will be three directions of particular importance; in one of these the colour will become stronger or weaker (depending on whether a forward or backward motion is made), in another the colour will become greener or redder, and in the third brighter or duller. In any other direction the colour will vary in more than one attribute. If only very small colour difference movements are made, these directions will be constant, and the colour difference from the standard colour will be directly proportional to the distance travelled. The colour of the standard may be regarded as the mathematical origin of a set of co-ordinates Δx, Δy, ΔY in colour space, and the three main directions of strength, shade, and brightness variations may be treated as straight lines passing through the origin (Fig. 2). The equations of these straight lines are given below.

$$\left.\begin{aligned} \Delta x/l_1 = \Delta y/m_1 = \Delta Y/n_1 &= \Delta S \text{ for strength} \\ \Delta x/l_2 = \Delta y/m_2 = \Delta Y/n_2 &= \Delta G \text{ for shade} \\ \Delta x/l_3 = \Delta y/m_3 = \Delta Y/n_3 &= \Delta B \text{ for brightness} \end{aligned}\right\} \quad \ldots\ldots (6)$$

Strictly, the equations of the straight lines are given by the ratio $l : m : n$. In Eqn. 6 the magnitudes of the constants have been included so that the distance along the line corresponding to one trace is defined. The equation of the shaded plane of Fig. 2 containing the lines of variable shade and brightness, i.e. the plane of zero strength difference, can be calculated to be

$$\begin{vmatrix} m_2 & n_2 \\ m_3 & n_3 \end{vmatrix} . \Delta x - \begin{vmatrix} l_1 & n_2 \\ l_3 & n_3 \end{vmatrix} . \Delta y + \begin{vmatrix} l_2 & m_2 \\ l_3 & m_3 \end{vmatrix} . \Delta Y = 0$$

It can also be shown that the plane parallel to this which cuts the line of variable strength at a point corresponding to ΔS traces is given by—

$$\Delta S = \frac{\begin{vmatrix} m_2 & n_2 \\ m_3 & n_3 \end{vmatrix} . \Delta x - \begin{vmatrix} l_2 & n_2 \\ l_3 & n_3 \end{vmatrix} . \Delta y + \begin{vmatrix} l_2 & m_2 \\ l_3 & m_3 \end{vmatrix} . \Delta Y}{\begin{vmatrix} l_1 & m_1 & n_1 \\ l_2 & m_2 & n_2 \\ l_3 & m_3 & n_3 \end{vmatrix}} \quad \ldots\ldots (7)$$

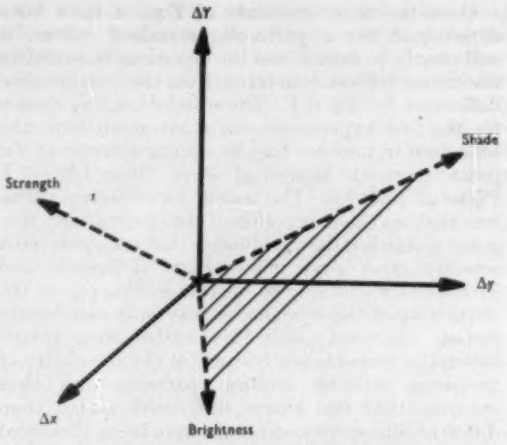

FIG. 2— Schematic representation of shade, strength, and brightness loci in colour space

It is therefore reasonable to assume that all the points in the vicinity of the standard point which lie on this plane have a strength difference of ΔS traces from the origin, no matter what the associated difference in shade or brightness may be. Eqn. 7 and two similar equations for shade and brightness are identical in form with Eqn. 4, although they now have the additional meaning of being the equations of planes of constant strength, shade, and brightness in colour space. The nine values of l, m, and n can be calculated from Eqn. 5, and these give the directions in colour space of the lines along which only strength, shade, and brightness vary. The projections of these lines on the chromaticity diagram are shown in Fig. 3.

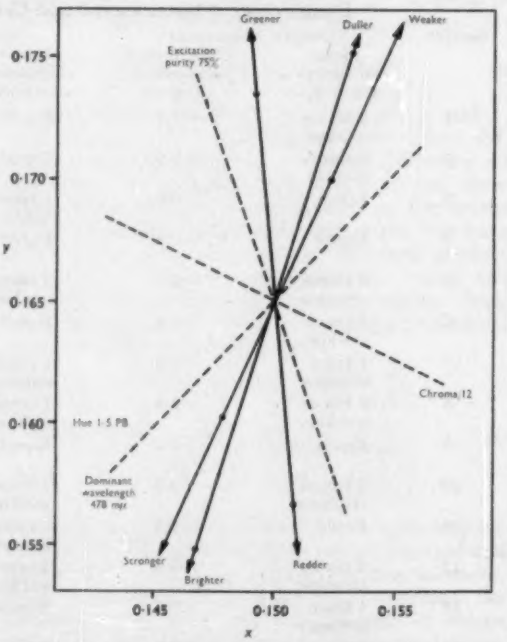

FIG. 3— Comparison of strength, shade, and brightness loci with other colorimetric parameters

It was stated earlier that conventional colorimetric variables do not correspond with the colourist's variables and give results which differ from those based on visual examination. On Fig. 3 are drawn lines of constant purity and dominant wavelength, which are two commonly used colorimetric variables, and also the lines of constant chroma and hue, which are two of the variables of the Munsell system. None of these lines corresponds even closely with the directions of the lines representing the colourist's variables. In fact, by using Eqn. 5 it can be shown that, for colour differences from the standard blue—

1 Munsell Hue step	= 6·4 traces weak, 7·0 traces red, 1·5 traces dull
1 Munsell Chroma step	= 7·6 traces weak, 6·4 traces red, 5·4 traces dull
1 Munsell Value step	= 11·6 traces weak, 2·2 traces green, 7·0 traces bright

Clearly there is no resemblance between the Munsell variables and the variables of strength, shade, and brightness.

It is also interesting to note that a colour variation involving a change in luminance but with no change in chromaticity produces a visual change in both strength and brightness, with a little change in hue. It would therefore be impossible for any instrumental system to use luminance as one of the colour attributes and at the same time have its attributes identical with the colourist's variables.

The widely accepted unit of total colour difference, the N.B.S. unit, which is used by some industries as the unit of colour tolerance for commercial matches, compares with the trace at this point of colour space as follows—

1 trace of strength difference	= 0·47 N.B.S. units
1 trace of shade difference	= 0·75 N.B.S. units
1 trace of brightness difference	= 0·84 N.B.S. units

This agreement between the trace and the N.B.S. unit is not very good, and for the six other colour standards that so far have been investigated in this way, no better agreement has been found.

The correlation between instrument readings and colourist's assessments has now been established about seven different coloured centres, representing saturated blue, green, yellow, orange, and scarlet, and a weaker orange and scarlet. In all cases it proved possible to represent traces of difference in colourist's attributes by linear equations of the type of Eqn. 4, with different values of the coefficients at each centre. It may be concluded that a direct translation from instrument readings into colourist's terminology can be established at any point in colour space, and that in measurements on regular surfaces, e.g. the paint films used in this work, the precision of the Colormaster equals or exceeds that of single colour assessments.

THE PHYSICS OF SUBTRACTIVE COLOUR MIXTURES AND THE PREDICTION OF COLOUR MATCHES

The experimental work described above is proof that instrumental measurement can replace to an adequate degree of precision that part of the colourist's skill which is concerned with describing colour differences in quantitative terms. It is now necessary to consider how far instrumental results may be used to replace that part of the colourist's skill which is concerned with removing by recipe adjustment the differences he has described. The approach used to solve this problem also gives a basis for formulating the first trial recipe for dyeing a match which has not previously been made, so that it is convenient to consider this aspect of the colourist's work at the same time.

Relationship between Dye Concentration and Monochromatic Reflectance

A solution to this problem must clearly be based on a relation between the reflecting properties of a dyed textile material and the concentration of dyes applied to it. Several theoretical expressions have been developed for expressing the reflectance of material in which both scattering and absorption are occurring, of which the best known is probably that due to Kubelka and Munk [15]. Their formulae were modified by Atherton [16] for the case of collimated incident light, a condition which applies to both the spectrophotometer and the colorimeter used in this work. For a dye on textile substrates, other assumptions may be made which further simplify the expressions to be used: it may be assumed that scattering is due to the substrate alone and that monochromatic absorption by the dye is proportional to the concentration of dye present. The relation between reflectance by a textile material at wavelength λ and the concentration of dye which it contains may then be expressed by—

$$\left(\frac{1}{R_\lambda}\right) = \left(\frac{1}{R_\lambda}\right)_s + \alpha_\lambda c \qquad \ldots\ (8)$$

where R_λ is the monochromatic reflectance of the dyed material at wavelength λ, $(R_\lambda)_s$ is the corresponding reflectance of the undyed substrate, c is the concentration of dye, and α_λ is the absorption coefficient characteristic of the particular dye used. When more than one dye is present, additional terms of form αc may be added to take account of this, and for the general case of interest in colour matching where three dyes are present, the equation takes the form—

$$\left(\frac{1}{R_\lambda}\right) = \left(\frac{1}{R_\lambda}\right)_s + \alpha_{\lambda_1} c_1 + \alpha_{\lambda_2} c_2 + \alpha_{\lambda_3} c_3 \qquad \ldots\ (9)$$

The validity of Eqn. 8 may be checked, and values of α_λ determined, by carrying out dyeings over a range of concentrations and determining the full spectral reflectance curve of each one. Similarly the applicability of Eqn. 9 may be checked from mixture dyeings where α_λ values have previously been determined in this way for the single dyes used as components in the mixture. Early experimental work [16] to test these equations, and the methods of match prediction derived from them, was carried out using level-dyeing acid dyes on wool flannel, and in this system they provided an adequate representation of the effects of dye concentration on reflectance. In later work on other dyeing systems, using the digital computer technique described below, it proved advantageous to use a more complex relation between reflectance and concentration, but the simpler Eqn. 8 and 9 will serve

adequately to describe the methods of match prediction which have been developed.

Methods of Match Prediction based on Measurements of Reflectance Curves

It is apparent that if the pattern to be matched is measured on a spectrophotometer and the monochromatic reflectance at three different wavelengths determined, Eqn. 9 may be written out for each of these wavelengths with the measured R_λ values and the known values of $(R_\lambda)_s$ and of α_{λ_1}, α_{λ_2} and α_{λ_3} for the dyes chosen to attempt the match. This will give three simultaneous equations which may be solved for the three concentrations c_1, c_2, and c_3, to give a recipe for a matching. Provided the same dyes are used to attempt the match as were used to dye the pattern to be matched, this simple technique works quite well. In the more general case, however, when different dyes are used, the shape of the reflectance curves of the unknown sample and of the attempted matching will differ, and the predicted concentrations will clearly depend on the wavelengths chosen to set up the equations. A good match will not generally be obtained from an arbitrary choice of wavelengths. As would be expected, therefore, the method is of limited utility as a general matching technique.

A refinement of the same technique may be made which requires the use of an analogue computer. This approach has been described by Atherton [16]. It consists in setting up on the computer the complete reciprocal reflectance curve of the pattern to be matched, and also a synthetic curve of the same kind based on Eqn. 9 from the known α_λ values of the dyes used to attempt the match. The shape and height of the second curve can be modified by adjustment of the three "concentration" controls on the computer until the best overall fit between the two curves is obtained, when the settings of concentration to achieve this condition will again be an indication of the matching recipe. The method eliminates the need to make an arbitrary choice of three wavelengths, and the operator can use his own judgment to assess the relative importance of deviations between the two curves when these are not of identical shape. As a consequence, better matches are possible than are given by the three-wavelength method in these circumstances, but the method still does not give an unambiguous prediction of the best recipe. A much more refined and accurate instrument operating on the same lines is the COMIC computer made by Davidson and Hemmendinger in U.S.A.

Methods of Match Prediction based on Tristimulus Values

These drawbacks to the foregoing methods, which would be expected on theoretical grounds and which are confirmed by experiment, arise essentially from a neglect of the eye's characteristic of synthesising an overall colour sensation from the mixture of radiations which it receives. The CIE system does in fact allow for this, and it is logical therefore to seek an improved method of match prediction by determining the concentrations necessary to produce a dyeing having the same tristimulus values in a particular illuminant as the pattern to be matched. This approach requires some further manipulation of Eqn. 9, which may be re-written—

$$R_\lambda = \frac{1}{(1/R_\lambda)_s + \alpha_{\lambda_1}c_1 + \alpha_{\lambda_2}c_2 + \alpha_{\lambda_3}c_3} \quad \ldots . (10)$$

The defining equations for the tristimulus values have been quoted in an earlier section and may be repeated here with the theoretical value of R_λ, as given by Eqn. 10, inserted.

$$\left.\begin{aligned} X &= \int \frac{E_\lambda.\bar{x}_\lambda.\mathrm{d}\lambda}{(1/R_\lambda)_s + \alpha_{\lambda_1}c_1 + \alpha_{\lambda_2}c_2 + \alpha_{\lambda_3}c_3} \\ Y &= \int \frac{E_\lambda.\bar{y}_\lambda.\mathrm{d}\lambda}{(1/R_\lambda)_s + \alpha_{\lambda_1}c_1 + \alpha_{\lambda_2}c_2 + \alpha_{\lambda_3}c_3} \\ Z &= \int \frac{E_\lambda.\bar{z}_\lambda.\mathrm{d}\lambda}{(1/R_\lambda)_s + \alpha_{\lambda_1}c_1 + \alpha_{\lambda_2}c_2 + \alpha_{\lambda_3}c_3} \end{aligned}\right\} \quad \ldots . (11)$$

All the factors on the right-hand sides of Eqn. 11, except the concentrations, are known for a particular three-dye combination. Consequently, if the measured values of X, Y, and Z for the pattern to be matched are inserted on the left-hand sides, it is possible in principle to solve the three equations for the three unknown concentrations. However, in practice this can be done only by a method of successive approximations, and the labour involved by conventional computational techniques is prohibitively large. For this reason no attempt was made, so far as is known, to use this method until high-speed digital computers became available.

Given such a computer, however, Eqn. 11 may be rapidly solved to give the dye concentrations for a first trial dyeing. At the same time the computer can also calculate from the same data partial differentials of the form $(\partial c_1/\partial X)$, $(\partial c_1/\partial Y)$, $(\partial c_1/\partial Z)$, and similarly for c_2 and c_3. These coefficients are mathematical expressions of the way in which the concentrations of the various dyes change with the position in X, Y, Z space of the point representing the calculated colour match. Over small volumes of colour space these coefficients will be essentially constant. Thus, if the trial dyeing from the first computed colour match proves on subsequent colour measurement to be in error from the required colour by increments ΔX, ΔY, and ΔZ, it is possible to compute the corrections $(\Delta c_1, \Delta c_2, \Delta c_3)$ which must be made to the recipe, with nothing more complicated than a slide rule. It should be noted particularly that after the first recipe and the nine coefficients have been computed, corrections can be made *without* further recourse to the computer.

Correction is made by use of the equations—

$$\left.\begin{aligned} \Delta c_1 &= \left(\frac{\partial c_1}{\partial X}\right).\Delta X + \left(\frac{\partial c_1}{\partial Y}\right).\Delta Y + \left(\frac{\partial c_1}{\partial Z}\right).\Delta Z \\ \Delta c_2 &= \left(\frac{\partial c_2}{\partial X}\right).\Delta X + \left(\frac{\partial c_2}{\partial Y}\right).\Delta Y + \left(\frac{\partial c_2}{\partial Z}\right).\Delta Z \\ \Delta c_3 &= \left(\frac{\partial c_3}{\partial X}\right).\Delta X + \left(\frac{\partial c_3}{\partial Y}\right).\Delta Y + \left(\frac{\partial c_3}{\partial Z}\right).\Delta Z \end{aligned}\right\} \quad \ldots . (12)$$

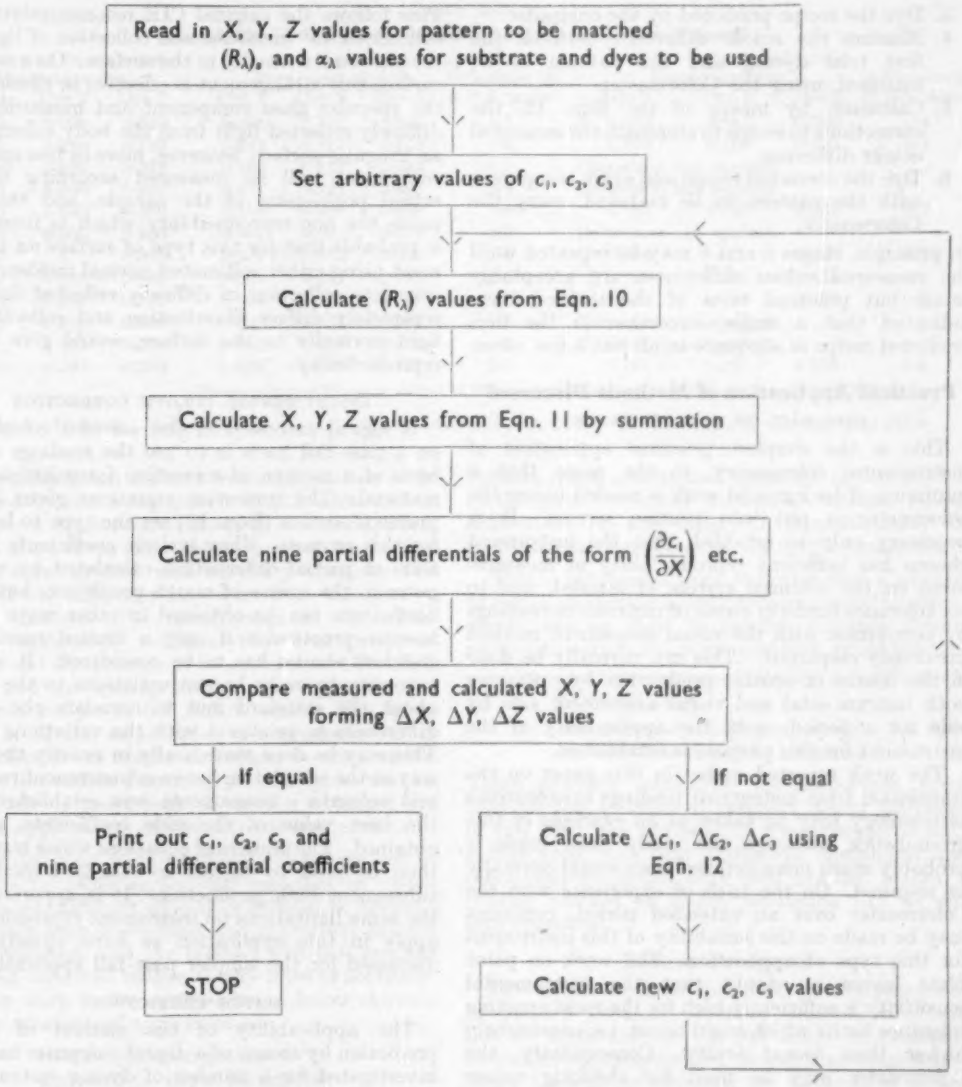
Read in X, Y, Z values for pattern to be matched
(Rλ), and αλ values for substrate and dyes to be used
Set arbitrary values of c1, c2, c3
Calculate (Rλ) values from Eqn. 10
Calculate X, Y, Z values from Eqn. 11 by summation
Calculate nine partial differentials of the form (∂ci/∂X) etc.
Compare measured and calculated X, Y, Z values
forming ΔX, ΔY, ΔZ values
If equal
If not equal
Print out c1, c2, c3 and
nine partial differential coefficients
Calculate Δc1, Δc2, Δc3 using
Eqn. 12
STOP
Calculate new c1, c2, c3 values

FIG. 4— Simplified computer flow diagram for match-prediction programme

These equations are based on analogous assumptions to those given earlier to relate visual and instrumental colour difference assessments, and their use is restricted to small colour differences for which the neglect of higher-order differentials than the first is justified. This assumption has been justified by practical experience of the method.

The method of calculating the three concentrations and nine partial differentials may be illustrated by the simplified computer flow diagram of Fig. 4. This serves also to emphasise again the enormous amount of arithmetic involved in carrying out this calculation. It will be seen that the partial differentials needed for the instrumental correction to the first trial dyeing recipe are also used within the computer programme itself in the method of successive approximations on which the programme operates.

This method of match prediction may be recapitulated by setting down in a step-wise manner the sequence of operations. This assumes that a complete library of standard data on the individual dyes and substrates to be used has been obtained in advance; this information needs measuring and recording only once.

1. Measure X, Y, and Z of the pattern to be matched on the Colormaster differential colorimeter.
2. Feed to the computer these values, together with the standard reflectance data for the substrate and dyes selected to attempt the match.

3. Dye the recipe predicted by the computer.
4. Measure the colour difference between the first trial dyeing and the pattern to be matched, using the Colormaster.
5. Calculate, by means of the Eqn. 12, the corrections to recipe to eliminate the measured colour difference.
6. Dye the corrected recipe and again compare it with the pattern to be matched, using the Colormaster.

In principle, stages 5 and 6 may be repeated until the measured colour differences are acceptably small, but practical tests of the method have indicated that a single correction to the first predicted recipe is adequate in all but a few cases.

Practical Application of Methods Discussed

PASS–FAIL ON COLOUR MATCH

This is the simplest practical application of instrumental colorimetry, in the sense that a minimum of background work is needed before the colorimeter is put into routine service. It is necessary only to establish that the instrument chosen has sufficient reproducibility of measurement on the coloured system of interest, and to set tolerance limits in terms of instrument readings by correlation with the visual assessment method previously employed. This can normally be done in the course of routine production by operating both instrumental and visual assessment side by side for a period, until the applicability of the instrument for this purpose is established.

The work reported earlier in this paper on the translation from instrument readings to colourist's terminology may be taken as an example of this groundwork, although the study there made is probably much more detailed than would normally be required. On the basis of experience with the Colormaster over an extended period, comment may be made on the suitability of this instrument for this type of application. The work on paint films leaves no doubt that the instrumental sensitivity is sufficiently high for the most exacting tolerance limits which could be set, i.e. consistently higher than visual acuity. Consequently, the Colormaster may be used for checking colour tolerance in paint systems, and in other applications where the coloured surface to be measured is of sufficient regularity, e.g. smooth coloured plastics. Unfortunately, reservations must be made about comparable applications of this instrument to woven textile materials. It is our experience that here the reproducibility of measurement of colour difference is considerably lower, so that the reproducibility of instrument readings is somewhat less than that of skilled visual assessment. This appears to be due entirely to the effects of surface irregularities, which can cause point-to-point and orientation differences in instrument readings on textile materials without causing similar discrepancies in visual assessments. Thus, the Colormaster is not as useful on such materials when tolerances to the limit of visual acuity must be set.

It is probable that this comparative deficiency in the Colormaster is due in part at least to the viewing geometry which the instrument employs. This follows the original CIE recommendation of collimated 45° incidence and collection of light by the photocell normally to the surface. On a smooth surface this arrangement is effective in eliminating the specular gloss component and measuring the diffusely reflected light from the body colour. On an irregular surface, however, more or less specular component will be measured according to the actual positioning of the sample, and this will cause the non-reproducibility which is found. It is probable that for this type of surface an instrument using either collimated normal incidence and complete collection of diffusely reflected light, or completely diffuse illumination and collection of light normally to the surface, would give better reproducibility.

INSTRUMENTAL COLOUR CORRECTION

A logical extension of the use of a colorimeter on a pass–fail basis is to use the readings as the basis of a method of correction for unsatisfactory material. The correction equations given in the previous section (Eqn. 12) are the type to be used for this purpose. They include coefficients in the form of partial differentials calculated by a computer in the course of match prediction, but these coefficients can be obtained in other ways which become practicable if only a limited number of standard shades has to be considered. It is then necessary to make known variations to the recipe about the standard and to correlate the colour differences so produced with the variations made. This may be done statistically in exactly the same way as the correlation between instrument readings and colourist's assessments was established, and the best value of the nine coefficients will be obtained. The numerical equations which result can then be used to correct to standard quality in subsequent bulk production. It is apparent that the same limitations on instrument reproducibility apply in this application as have already been discussed for the simpler pass–fail application.

MATCH PREDICTION

The applicability of the method of match prediction by means of a digital computer has been investigated for a number of dyeing systems, the most thorough study having been made of level-dyeing acid dyes on wool flannel. For this system the reflectance–concentration relationship of Eqn. 9 was used, but the accuracy of first matching was improved by replacing the CIE response functions $\bar{x}_\lambda$, $\bar{y}_\lambda$, $\bar{z}_\lambda$ of Eqn. 11 by functions determined experimentally for the lamp–filter–photocell combinations of the particular Colormaster instrument used. With this modification the procedure adopted was exactly as outlined in the previous section, integration at 32 ordinates being used to evaluate Eqn. 11.

Typical results obtained are illustrated in Table III. For purposes of illustration examples have been chosen in which the same dyes were used to attempt the match as had been used in dyeing the pattern to be matched, since it is then possible to compare the predicted recipes with the correct ones, as well as to compare the colour differences produced. Five of the twelve first-dyeing recipes

TABLE III

Match Prediction— Level-dyeing Acid Dyes on Wool Flannel

Pattern to be matched			First predicted recipe				Corrected recipe			
Percentage dye			Percentage dye			Difference in	Percentage dye			Difference in
Dye 1	Dye 2	Dye 3	Dye 1	Dye 2	Dye 3	N.B.S. units	Dye 1	Dye 2	Dye 3	N.B.S. units
0·050	0·700	0·040	0·053	0·702	0·046	1·7	0·052	0·681	0·040	0·4
0·100	0·200	0·120	0·112	0·217	0·132	1·6	0·100	0·195	0·121	0·5
0·250	0·250	0·030	0·246	0·252	0·033	0·9	Correction not applied			
0·900	0·800	0·400	0·881	0·795	0·407	0·4	Correction not applied			
0·800	0·030	0·050	0·818	0·036	0·059	2·8	0·789	0·028	0·052	0·7
0·300	0·200	0·230	0·301	0·190	0·223	0·9	Correction not applied			
0·300	0	0·300	0·327	(−0·005)	0·301	1·6	0·308	—	0·289	1·1
0·700	0·200	0·800	0·668	0·162	0·745	2·6	0·700	0·206	0·822	0·9
0·050	0·030	0·700	0·045	0·007	0·701	1·9	0·052	0·039	0·690	0·6
0·300	0·300	0·400	0·300	0·286	0·394	0·7	Correction not applied			
0	0·200	0·200	0·001	0·210	0·211	1·0	Correction not applied			
0·200	0·200	0·200	0·234	0·219	0·227	2·0	0·191	0·197	0·190	0·4
			Mean colour difference = 1·5 N.B.S. units				Mean colour difference = 0·7 N.B.S. units			

Dye 1 Lissamine Yellow 2GS *Dye 2* Azo Geranine 2GS *Dye 3* Solway Blue BNS

gave results which differed from the pattern to be matched by not more than 1 N.B.S. unit, and in these cases the correction formula was not applied. In the other seven cases the corrections to the first recipe were applied and in every instance this reduced the difference in colour from the pattern to be matched. The mean value of the overall colour differences between the first predicted recipes and the pattern to be matched is 1·5 N.B.S. units, and the corresponding mean figure for the corrected recipes is 0·7 N.B.S. units. The latter value is of the same order of reproducibility as measurement on textile materials, because of the surface limitations discussed previously, so that no significant improvement is to be obtained by further applications of the correction equations.

Provided that metameric differences are not so large as to cause significant variation in visual assessment, different dyes may be used to attempt the match from those used on the original pattern to be matched, and the method will still produce first and corrected recipes to this level of accuracy. Further work in the systems listed below shows a similar measure of agreement—

reactive dyes on cotton
pigments on paper laminates
pigments on viscose rayon
chrome dyes on wool.

In this part of the work it was found that a better representation of reflectance data was obtained by substituting for Eqn. 9 the more complex relation—

$$F(R_\lambda) = (1-R_\lambda)^2/(R_\lambda - R_0)\,(1+kR_\lambda)$$
$$= F(R_\lambda)_s + \alpha_{\lambda_1} c_1 + \alpha_{\lambda_2} c_2 + \alpha_{\lambda_3} c_3 \quad \ldots \quad (13)$$

This form of $F(R_\lambda)$ is suggested by Fink–Jensen [17] from a study of the work of Saunderson [18]. The constants R_0 and k take account of surface reflections, and are to be determined as best values for the particular fibre system under investigation. The use of this equation further complicates the form of Eqn. 11, but the additional arithmetic required for their solution is acceptable when a digital computer is being used. By means of Eqn. 13, first-matching recipes could again be predicted to about the accuracy indicated in Table II, for each of the systems listed above, and again the first corrected recipe gave, in most instances, residual colour differences of the order of reproducibility of instrumental measurement on textile materials.

This experimental work indicates that a method of match prediction based on instrumental measurements can be used to predict accurate dyeing recipes to match unknown patterns, provided that

(*a*) the necessary computational facilities are available, and

(*b*) the necessary background data on dyes and substrates can be acquired.

These provisos emphasise the important point that for the solution of complex colour problems of this kind, the purchase of a colorimeter is only a first step, and that additional equipment and much experimental work are needed before a routine method of match prediction can be put into operation.

Future Prospects

Few of the methods described in this paper are at present used in practice. Indeed, they are not all applicable to the full range of problems encountered in a dyehouse. Colour matchings sometimes have to be obtained for patterns of a size which is inadequate for colour measurement. Snap judgments based on the colour of partially dyed, wet material cannot be made by colorimeter with the same facility as by a human operator. Selection of dyes, being a complex exercise with technical and economic factors, is at present beyond the scope of the methods discussed here. No doubt the reader can augment this list of existing shortcomings of the instrumental method. Many of these will, however, be overcome by more elaborate computer techniques and more flexible measuring instruments.

The most significant advance that has been reported is the use of high-speed electronic computers for colour matching, and it is unfortunate that this method is one likely to arouse the most scepticism on the part of the practical dyer. Once a computer programme has been written, however, this method is extremely simple to use and has

much to offer in speed and economy. A computer of the type used in the present investigations may cost about £100,000 and could clearly not be justified for colour matching alone. It is possible, however, to hire time on such computers at an hourly rate of about £30, so that, assuming a running time of 30 seconds per problem, including print out, matchings may be obtained for 5s. 0d. each. It is not unreasonable to imagine a system in which the programme and data tapes of the various ranges of dyes are kept at the computer centre. Values of the colour co-ordinates to be matched and the serial numbers of the dyes to be used would be determined in a laboratory and transmitted by telephone, or preferably teleprinted (thus producing a tape capable of being fed into the computer). On completion of the calculation the output tape from the computer would be transmitted back to the laboratory, thus saving time on the output printer of the computer.

It is also clear that more complicated calculations are possible. For example, if data on the cost/lb of the various dyes are used, the economics of matching with different combinations of dyes can be studied.

Development along these lines will certainly proceed and need not, as colorimeters become more readily and cheaply available, be restricted to the larger dyeing firms. It must be stressed in conclusion, however, that no existing physical instruments are capable of exercising intelligent judgment and that the operation of instrumental colour control will for many years be no more reliable than its operator.

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References

1 McLaren, unpublished.
2 See e.g. Polyak, *The Retina* (Chicago: Chicago University Press, 1941).
Documenta Ophthalmologica, **III** (1949).
Wolff, *The Anatomy of the Eye and Orbit* (London: Lewis, 1954).
Granit, *Receptors and Sensory Perception* (New Haven: Yale University Press, 1955).
Dartnall, *The Visual Pigments* (London: Methuen, 1957).
3 Wright, *Trans. Opt. Soc.*, **30**, 141 (1928).
4 Guild, *Phil. Trans. Roy. Soc.*, **A230**, 149 (1931).
5 Commission Internationale d'Eclairage, *Compte Rendu*, p. 19 (1931).
6 Hardy, *J. Opt. Soc. Amer.*, **25**, 305 (1935).
7 Davidson and Imm, *ibid.*, **39**, 942 (1949).
8 Davidson and Godlove, *Amer. Dyestuff Rep.*, **39**, P78 (1950).
9 Hunter, *J. Opt. Soc. Amer.*, **38**, 661 (1948).
10 Stiles, *Optica Acta*, **2**, 168 (1955).
11 Glasser, *Aspects Théoretiques et Pratiques du Contretypage des Couleurs Congrès* FATIPEC **III**, 47 (1955).
12 Judd, *Amer. J. Psychol.*, **52**, 418 (1939).
Nat. Bur. Stand. Circular C429 (1942).
13 Munsell Colour Co., *The Munsell Book of Colour*.
14 McAdam, *J. Opt. Soc. Amer.*, **32**, 247 (1942).
15 Kubelka and Munk, *Z. Tech. Physik*, **12**, 593 (1931).
16 Atherton, J.S.D.C., **71**, 389 (1955).
17 Fink–Jensen, Ref. 11, p. 203.
18 Saunderson, *J. Opt. Soc. Amer.*, **32**, 727 (1942).

Discussion

Professor R. H. PETERS: Are any difficulties encountered in the choice of the primary colours? If the colour to be matched lies outside the colour gamut of the primaries, new ones must be chosen. Does this lead to any difficulties as far as metamerism is concerned? In other words, are there any limits on the choice?

Dr. ATHERTON: In cases where a problem is set up involving a colour outside the gamut of the dyes selected, the computer attempts to use a negative dye concentration. This is detected immediately and if it occurs on more than one iteration the calculation is summarily terminated and the inadequacy of the dyes is printed out by computer.

There are no limitations on the choice of dyes, subject to the above considerations, although certain combinations will give more freedom from metamerism than others in any particular case.

Professor PETERS: Which reflectance function do the authors consider the most suitable for this kind of work?

Mr. DERBYSHIRE: The reflectance function given as Eqn. 13 of the paper is now used in all development work on the computer technique. Because of the two disposable constants that the function contains, it can be used for all dye and fibre systems so far investigated, with a suitable choice of constants for each system to give the best representation of reflectance data. Consequently, a single general computer programme may be used for any dyeing system, with the appropriate values of the constants fed in on a parameter tape.

Mr. W. BEAL: Does the nature of the substrate of the pattern affect the accuracy of the system, in particular if this is very different from the substrate to be dyed, e.g. a pattern on glossy paper to be matched on wool?

Mr. DERBYSHIRE: The accuracy to which a match can be obtained by the instrumental technique is reduced if substrates of very different surface reflectance properties are used for the pattern to be matched and for the attempted matchings. In these circumstances a dyeing which gives identical instrumental readings to those from the pattern to be matched will not in general give the best visual match, so that a final adjustment to shade based on visual assessment will be more rewarding than repeated application of the instrumental correction equations. Even in these unfavourable conditions, however, the application of the computer technique for the first trial recipe is worthwhile, as this will give a closer approximation than would be obtained by traditional methods on the basis of a single dyeing.

Mr. I. GAILEY: Several times in the paper the relationships governing small changes in colour about standard colours are stated to be linear. What are the dimensions in colour space expressed in N.B.S. units about a standard colour over which these linear relationships hold?

Dr. ATHERTON: It is difficult to give an exact answer to this question, since the limits of linearity will vary with position in the colour solid. In our experience the functions used are substantially

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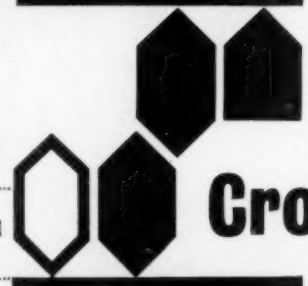

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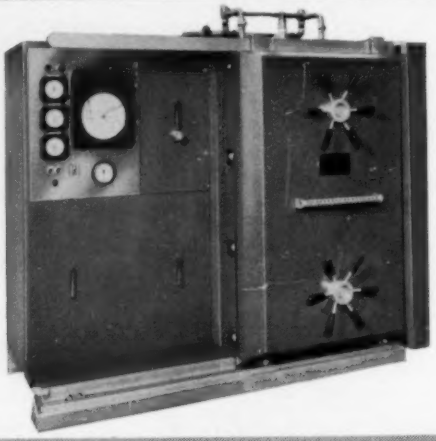

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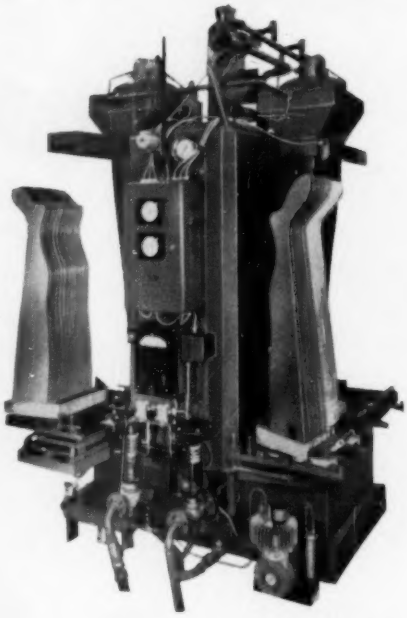

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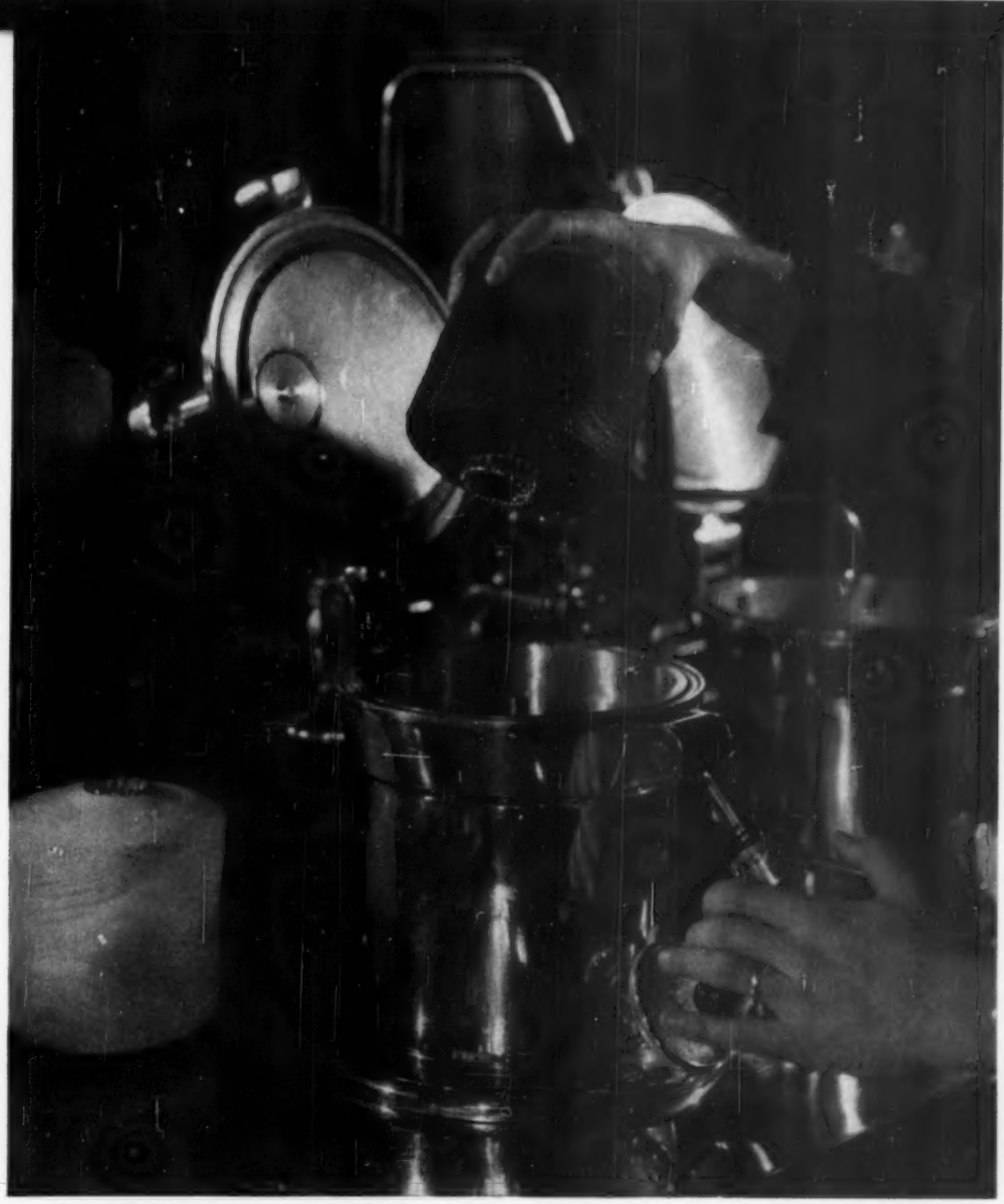

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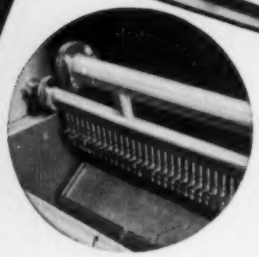

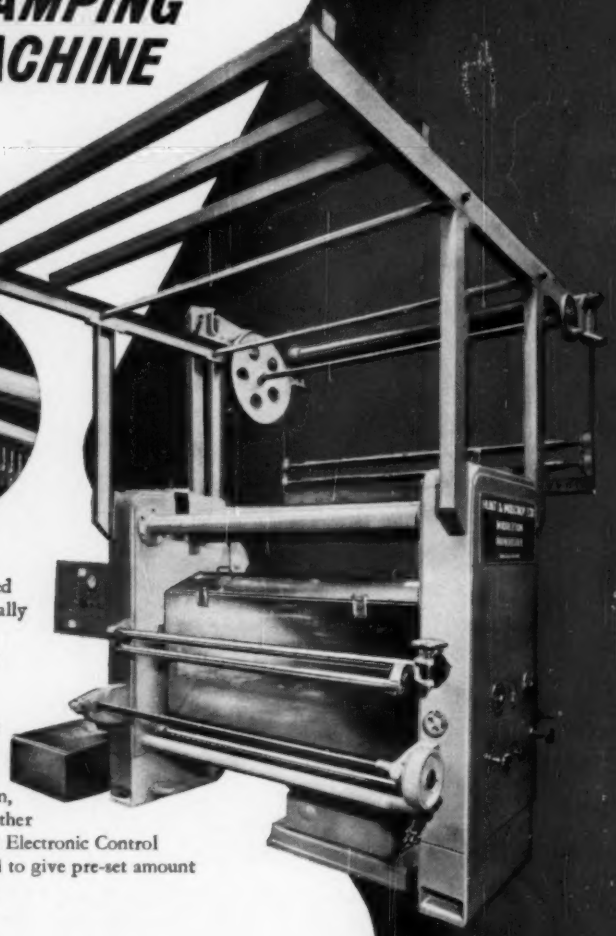

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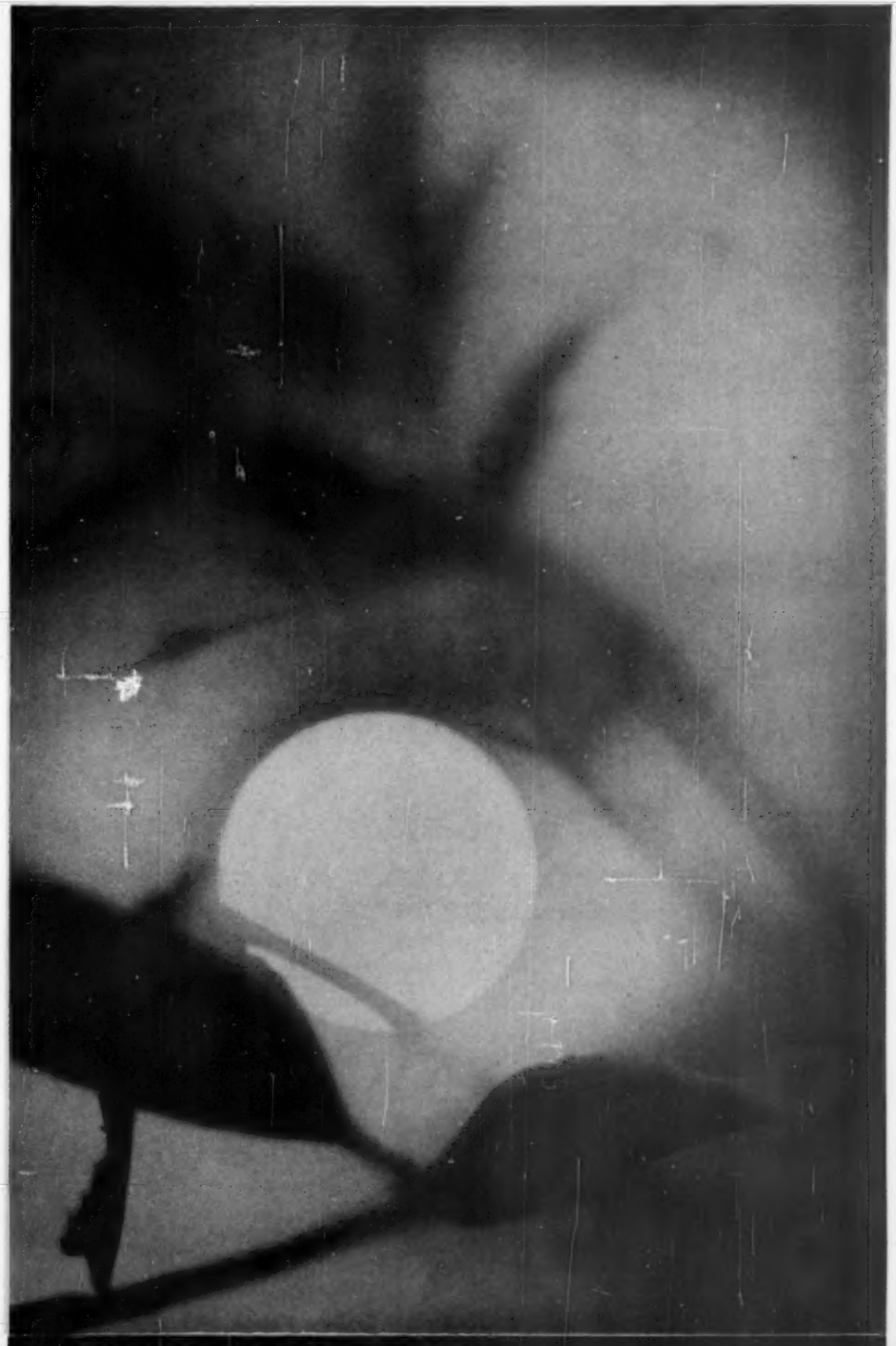
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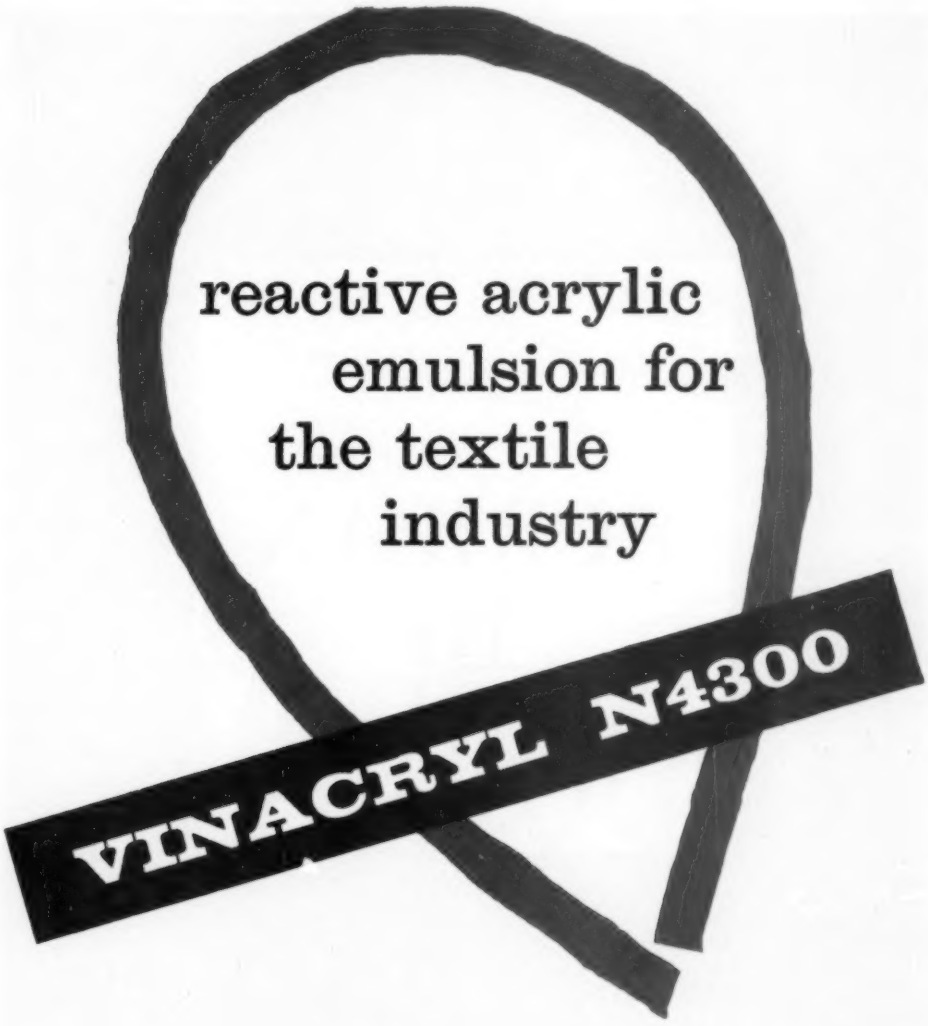

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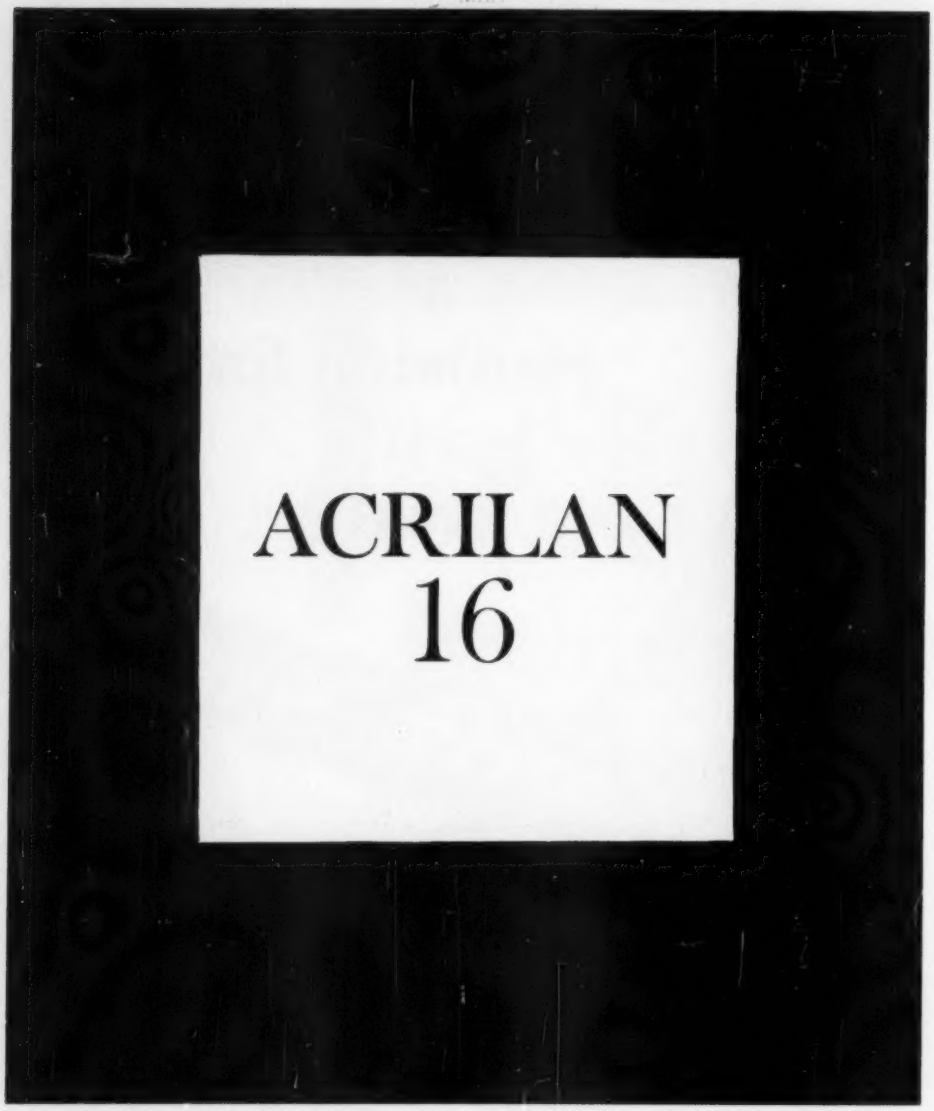

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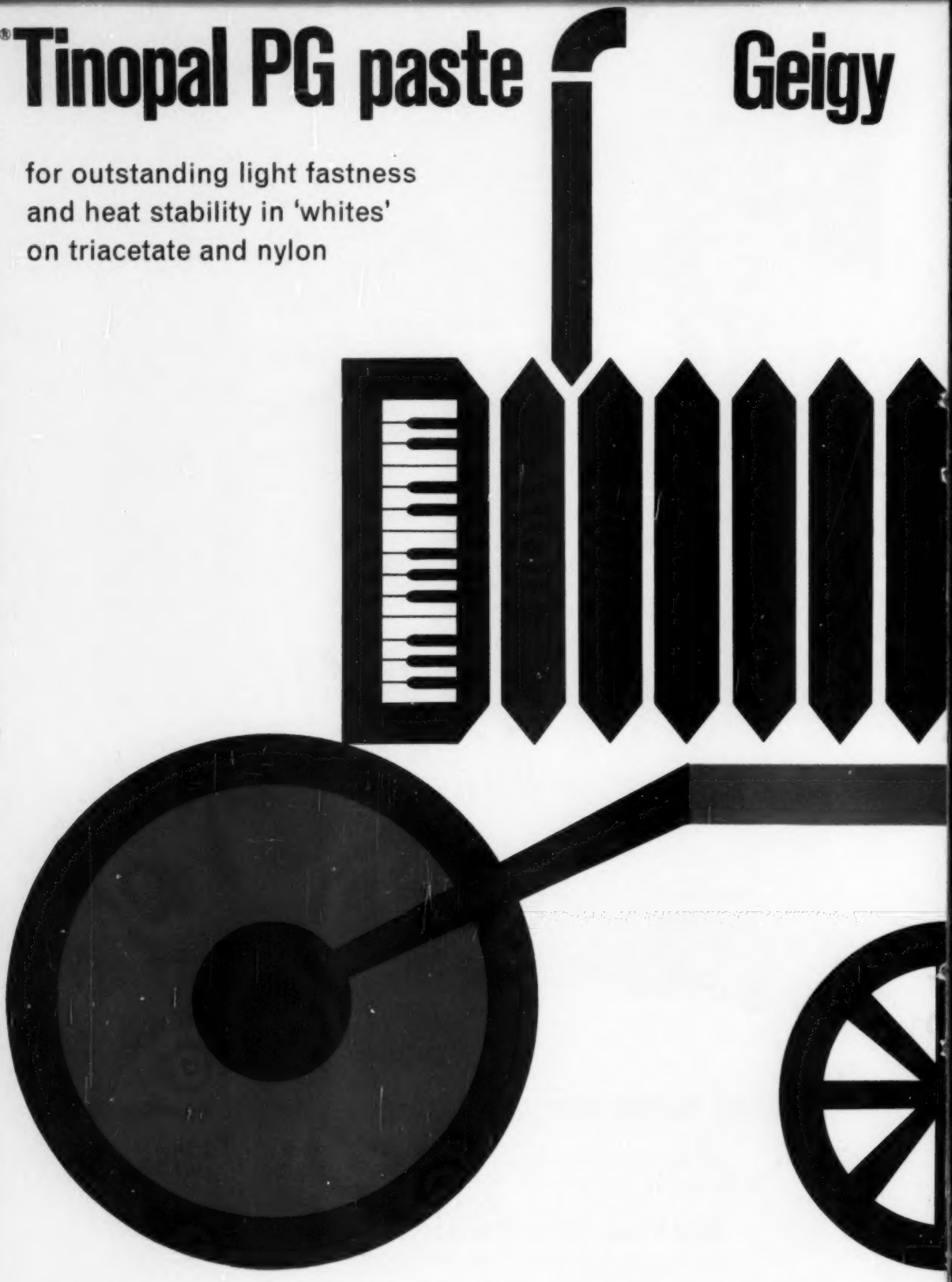

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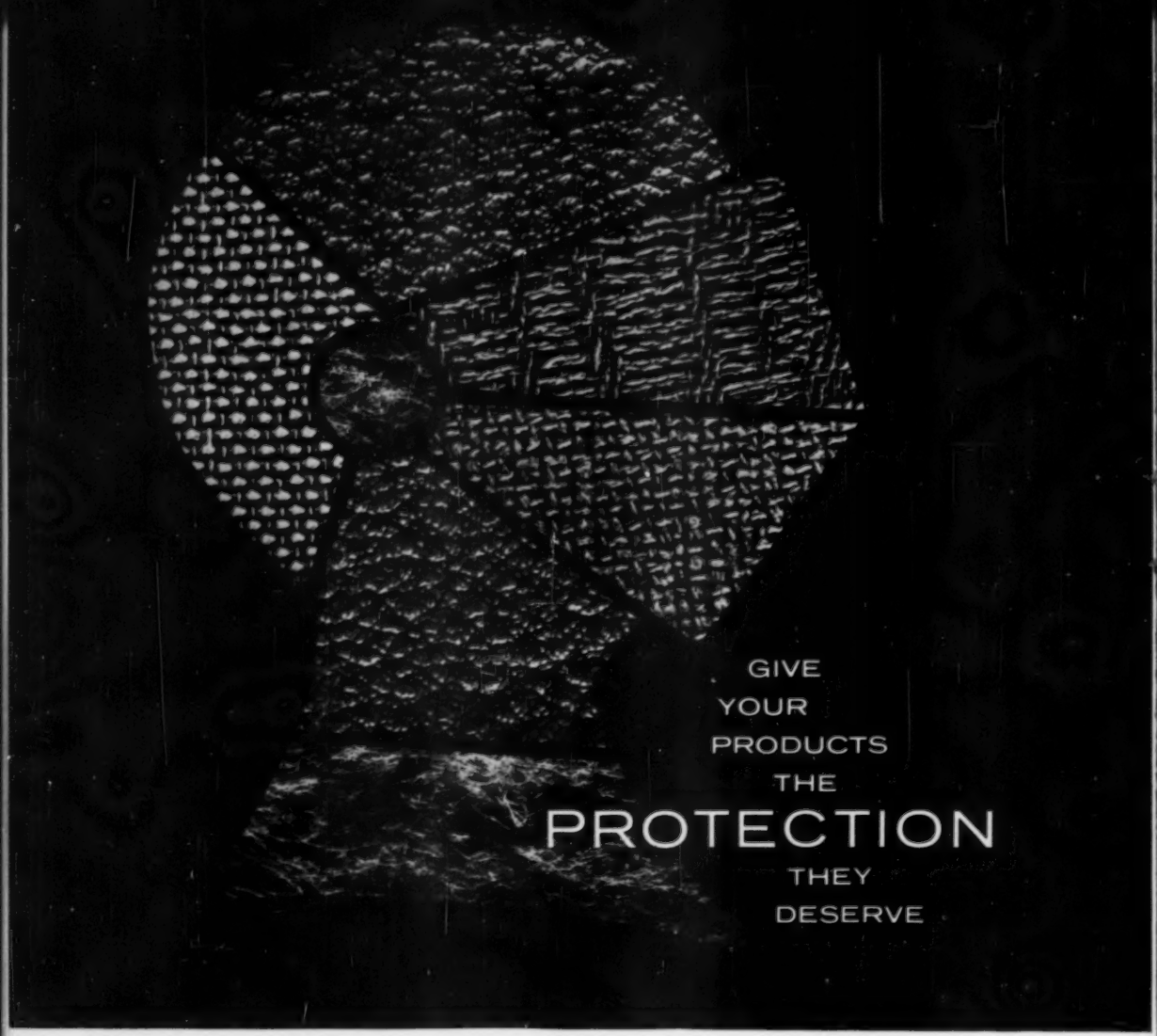

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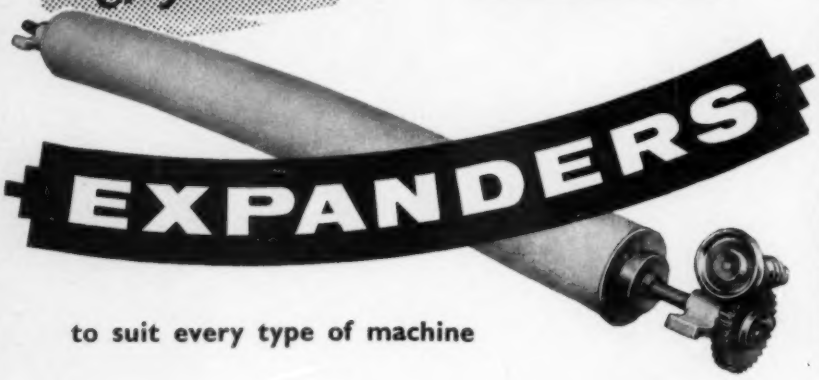

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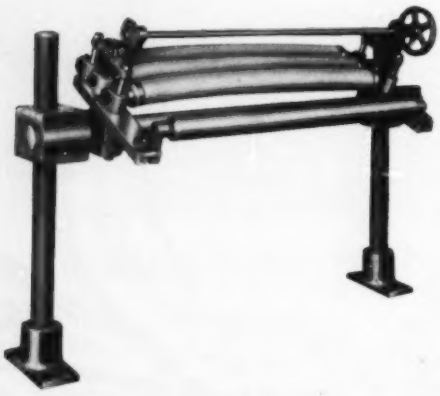

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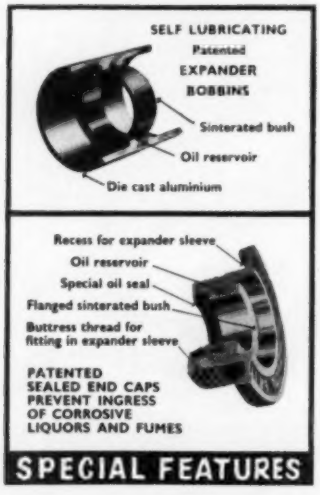

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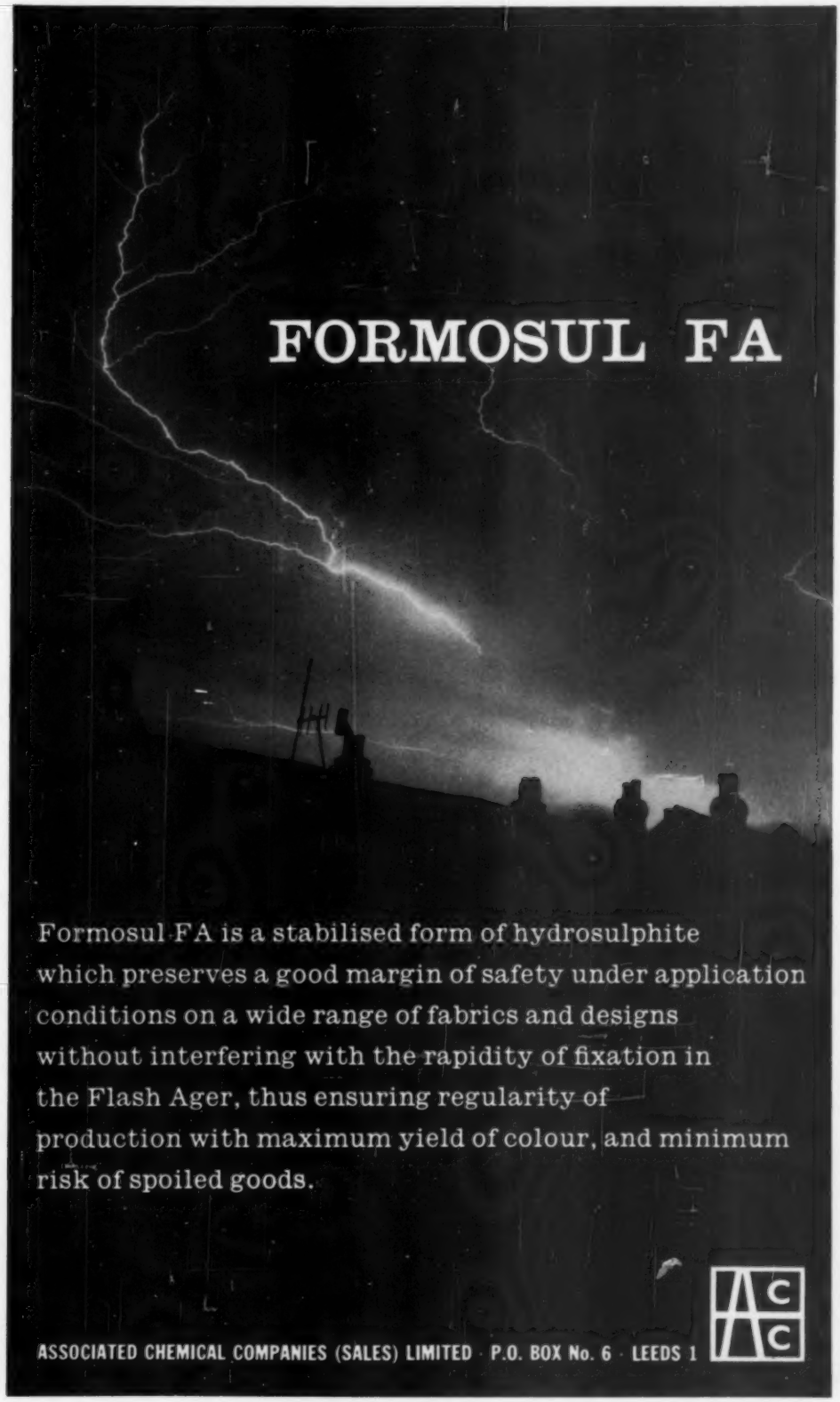
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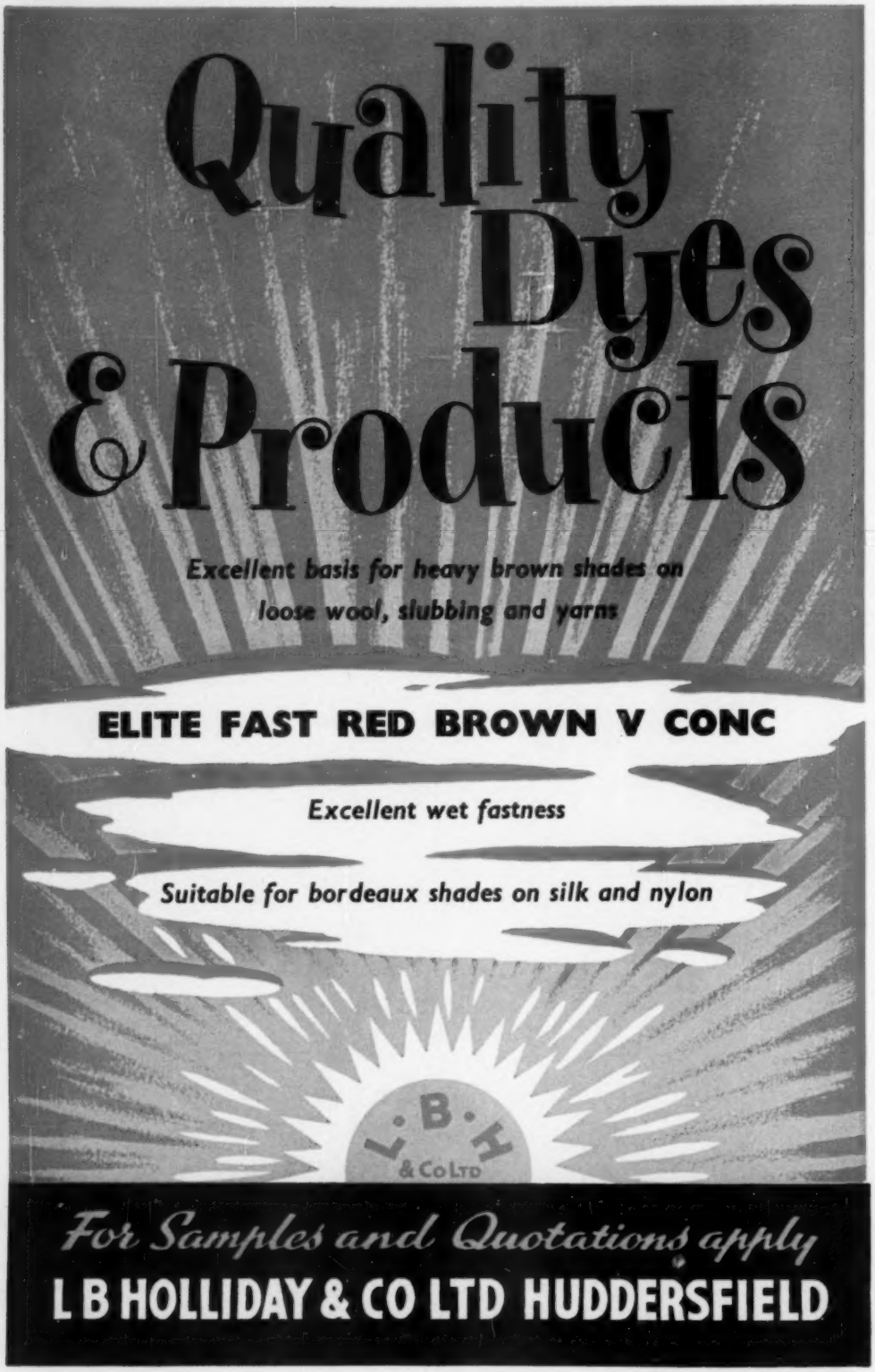
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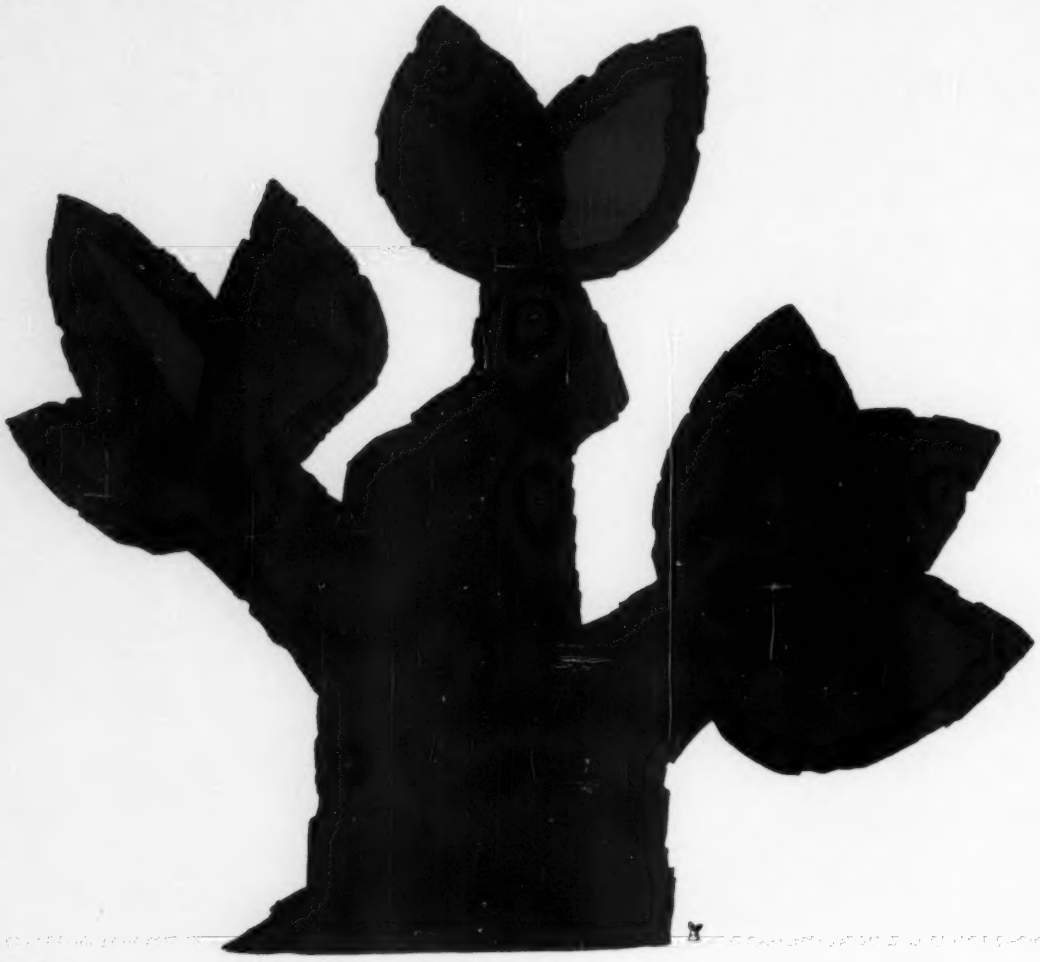

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linear up to 7 N.B.S. units from the reference colour.

Dr. J. K. SKELLY: Is a trichromatic filter instrument of the Colormaster type sufficiently accurate for colour matching over the whole gamut of colour, and is the accuracy not better in some regions of the colour solid than in others?

Dr. ATHERTON: The colorimetric accuracy of any trifilter colorimeter is variable over the colour ranges encountered in practice, but this is not of great significance in colour matching with an instrument of the high precision of the Colormaster. In the blue and violet region, where the eye is most sensitive to chromaticity change, the instrument has, in our experience, adequate sensitivity for the purposes described.

Mr. T. GREEN: The authors refer (on p. 666) to the determination of the CIE response functions for the lamp–filter–photocell combination of the particular Colormaster instrument used in this work. What method was used for this determination?

Mr. DERBYSHIRE: The colour temperature of the lamp used in the Colormaster was measured, and the energy output as a function of wavelength calculated assuming black-body radiation at this temperature. The filter transmissions as a function of wavelength were measured on both the G.E. Hardy Spectrophotometer and the Cary Recording Spectrophotometer. The relative outputs of the photocells were measured at 20 mμ intervals at the National Physical Laboratory.

Mr. T. FLANAGAN*: I can visualise this system working for weak depths where the degree of dyebath exhaustion is very high. However, fastness properties very often dictate the dyes to be used and the components of a mixture dyeing may not have the same exhaustion rates. In such cases equilibrium conditions for each component will differ. Would this have an effect on the accuracy of match prediction and correction?

Mr. ALDERSON*: The dyebath exhaustion need not necessarily be high for accurate predictions of the matching recipe; it is only when there is a marked falling off in percentage exhaustion at high concentrations that the prediction of dye concentration loses accuracy. These cases seldom seem to arise in practice, but when they do, the correction procedure can still be applied and will lead to a marked improvement in the colour match obtained.

Dr. G. H. LISTER*: The statistical determination of a dyeing recipe assumes either that 100% exhaustion of dye has been obtained for the standard pattern or that in the reproduction dyeing the identical percentage exhaustion of the dyebath will be obtained as that previously obtained in preparing the standard. Complete exhaustion of a dyebath means the use of dyeing and levelling conditions that are far from ideal. Alternatively, in order to reach an equilibrium exhaustion that is identical for standard and assessed recipe, exact control of various factors contributing to the equilibrium are required. Does not this represent a fundamental weakness in the instrumental determination of dyeing recipes?

Dr. ATHERTON*: The factors mentioned by Dr. Lister, when they occur, will reduce the accuracy of the first predicted recipe, but subsequent correction using the derivatives printed out with the recipe will produce a good match in all but the most incompatible dye mixtures. Even in these cases, further correction will produce an accurate match.

* Communicated

Control and Specification of Fluorescent Whites and Colours

J. M. ADAMS

Colorimeters of different manufacture will not, in general, give measurements agreeing with one another even though they are designed to conform to CIE specifications, and the reasons for this are summarised. The conditions that must be fulfilled by a colorimeter to be used for the measurement of fluorescent colours are given, and light sources that have been proposed for the colorimetry and visual assessment of fluorescent materials are reviewed and compared. Some of the methods of assessment that have been proposed are applicable only to fluorescently brightened near-whites.

Introduction

The deliberate use of fluorescent materials as colorants has for some years been accepted in the textile, paper, and printing ink industries, and much has been published on methods of assessing the contribution of the fluorescence to a colour and on the specification of fluorescent colours.

The aim of this paper is to summarise and compare these methods. Some general requirements of colour-measuring instruments are discussed, with particular reference to differences between instruments which, at present, make colour measurement an inadequate specification of a colour for general use. The main part of the paper is taken up with a review of light sources, both for instruments and for visual control, and spectral-energy curves are given for those which have been proposed for use with fluorescent colours. The provision of a light source which matches daylight throughout the visible and near ultraviolet regions of the spectrum seems to be the main problem in the control of fluorescent colours at present.

Most of the fluorescent colours used in practice are near-whites, in which the fluorescent dye absorbs only in the ultraviolet region and emits in the violet and blue regions. These lend themselves to specialised control techniques using fluorimeters, and there are ingenious methods of combining the ultraviolet-excited fluorescence with a colour measurement that does not include the fluorescent component.

Colour Measurements

Complete dependence on measurements of colour for control and specification is not yet practicable, owing to limitations imposed by the quality of the instruments available, which limits the accuracy with which standard conditions can be met, and also by the looseness of some of the standards to which the instruments are made. The CIE specifications for light-source and receptor characteristics are unambiguous [1], but it is not easy to reproduce them using the lamps, glass or gelatine filters, and photocells available to manufacturers of colorimeters, and departures from these standards will introduce errors in measurement, particularly with saturated colours. The other limitation set by the quality of the instrument is the precision with which the reflectance measurements on which the colour co-ordinates are based can be made. This limitation is particularly noticeable when working with near-white materials, for which trichromatic coefficients and luminance factors must be known to within 0·0005 and 0·3%, respectively, if just perceptibly different colours are to be distinguished [2].

The main source of error due to vagueness or non-observance of standards is the variation in illuminating and viewing conditions between instruments. The CIE recommendation is for illumination at 45° and viewing normally, or normal illumination and 45° viewing, and implies that these are equivalent. This is, of course, not so. But more important is the lack of any specification for the angles subtended by the illuminating and viewing apertures, and the use of completely different geometries by many instrument manufacturers. One criticism of the CIE conditions is the dependence of a colour measurement of a material having a textured surface on the orientation of the sample, and a variant of normal illumination with 45° viewing which avoids this criticism employs an annular photocell or mirror receiving a hollow cone of light from the sample, as shown in Fig. 1. In the paper industry it is usually considered desirable to avoid any dependence of a measurement on the surface structure of a sample.

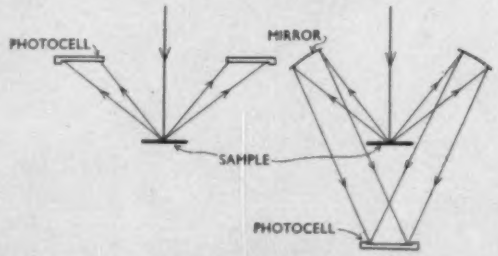

FIG. 1—Normal illumination and 45° viewing using an annular photocell or mirror

A positive reason for the adoption of non-CIE-standard illuminating and viewing conditions is that the Kubelka–Munk theory of diffuse reflection [3] is sometimes used to predict the colour of a material, and this theory assumes diffuse illumination of the material. It has been found that a colour-measuring instrument in which the sample is illuminated diffusely gives results in better agreement with the theory [4], as would be

expected, and it is likely that future standards for diffuse reflectance measurements will specify diffuse illumination and normal viewing [5].

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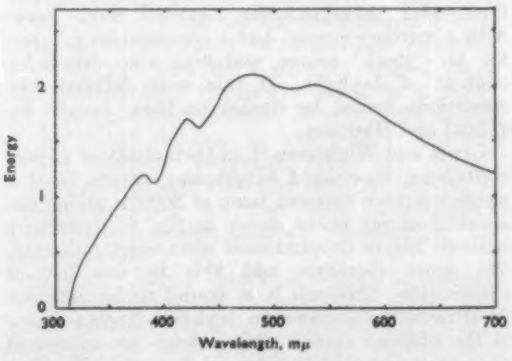

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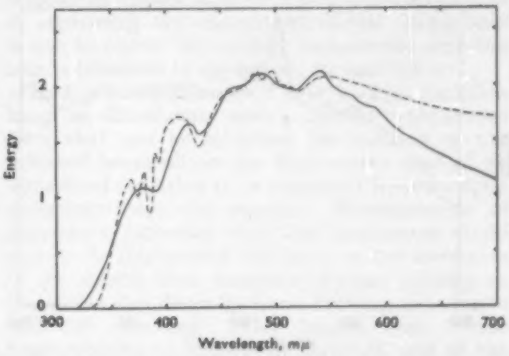

FIG. 3—Solid curve: Daylight seen through window glass, according to Herrmann; Dashed curve: Daylight indoors, according to Friele

appreciably. Also shown in Fig. 3 is a more recent measurement of daylight from an overcast sky seen through a window [8].

These may be taken as representative of the natural conditions under which materials may be seen, and much of the work involved in assessing fluorescent colours, both visually and by means of colorimeters, has been directed towards reproducing these conditions artificially.

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Thus, from a theoretical viewpoint, it would seem that the xenon arc provides a suitable source for the colorimetry of fluorescent materials, although in practice it has several shortcomings. It is expensive, and like all arc lamps it requires chokes or resistors to limit the arc current, and also a high-voltage pulse across the arc for starting. The most serious objection to its use for colorimetry is the difficulty of preventing the arc from wandering in the space between the electrodes. This causes instability in a single-beam colorimeter, and, although a lamp will settle down for short periods, I have now tried three examples of the German Osram (Neron) XBO 301 lamp in a Sheen abridged spectrophotometer [10] and made a few measurements using a Siemens GAE6 lamp, all operated on direct current, and have found none of them adequately stable. Conversations with others who have used this type of lamp indicate that this experience is general. It is possible to use an optical method to stabilise an image of the arc, but this would inevitably be fairly complicated. It is notable that the only commercially produced instrument employing a xenon arc lamp as a light source, the Elrepho, has an optical system giving

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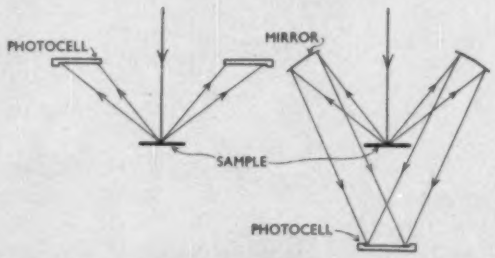

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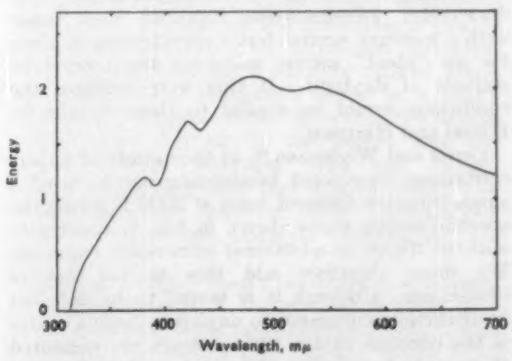

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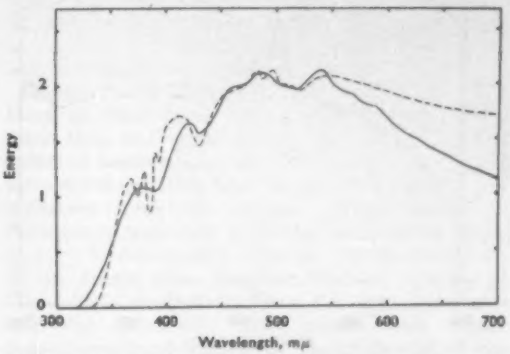

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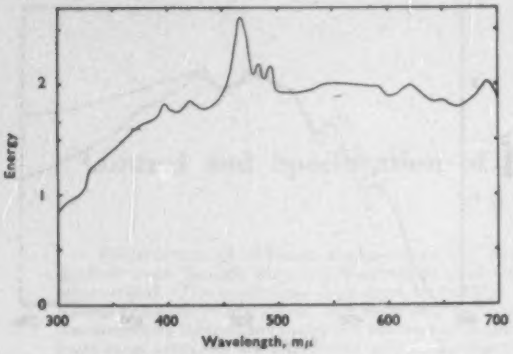

FIG. 4—Spectral-energy curve of xenon arc lamp

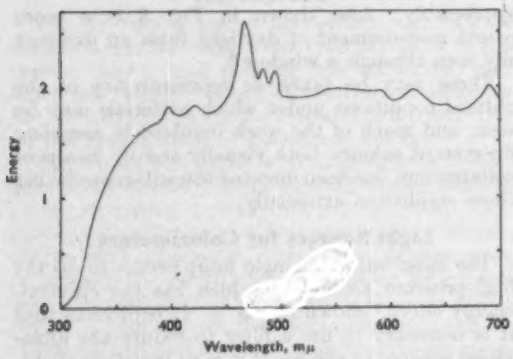

FIG. 5—Spectral-energy curve of xenon arc lamp with glass filter

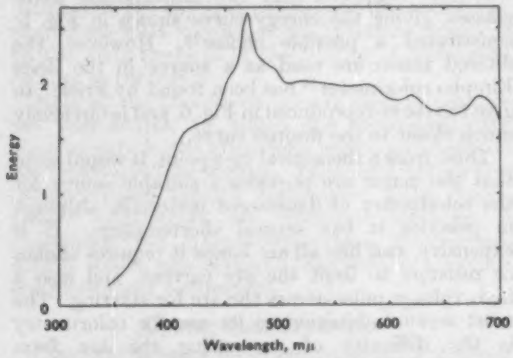

FIG. 6—Spectral-energy curve of source used in Elrepho colorimeter

simultaneous diffuse illumination of sample and reference standard, which are viewed by separate photocells. With this arrangement it could be expected that any fluctuations in the lamp would affect both photocells equally, and the reading remain stable.

A tungsten lamp with a suitable filter gives a source close to illuminant C, and it is a logical idea to retain this and supplement it by a source emitting ultraviolet radiation only. A suitable supplementary source is a filament lamp with an ultraviolet-transmitting filter[12,13]. The sample may be illuminated by both lamps simultaneously or, as in Harrison's colorimeter[14], the same lamp may provide both sources. In this case reflectance readings are taken with the sample illuminated by illuminant C (tungsten lamp with "daylight" filter) and then the daylight filter is replaced by the ultraviolet filter and further readings are taken. These are multiplied by an appropriate factor and added to the reflectance readings. This system results in a colorimeter that is only a little more complicated than one with no provision for measuring fluorescent colours, but the time required for making a measurement is increased.

The use of different ultraviolet filters and the alteration of the colour temperature of the lamp can modify the spectral-energy distribution considerably, as can be seen from Fig. 7, which shows the energy curves of the illuminants used by Hisdal and Harrison.

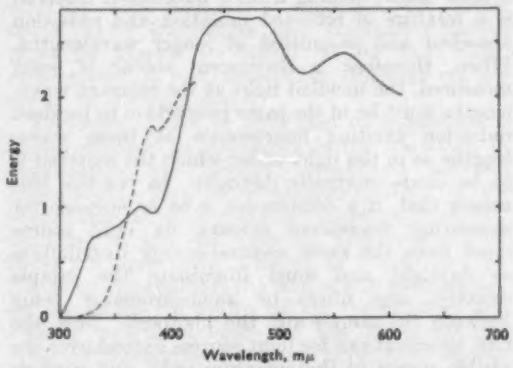

FIG. 7—Light sources proposed by Hisdal (solid) and by Harrison (dashed curve)

A further possibility is the use of a filtered mercury vapour lamp as the supplementary source. This effectively adds monochromatic radiation at 365·5 mμ (the line will be broadened and a continuum added if the lamp pressure is high) to the main source, and there seems little possibility of matching daylight with such a combination.

Another approach to the problem, which makes use of a supplementary ultraviolet source, is that of Allen[15,16], who combines a fluorimeter reading (a colour measurement of the fluorescence excited by ultraviolet radiation) with a colour measurement under illuminant C by calculating the additive colour mixture of the two measurements. The fluorimeter measurements reported were made with a mercury source, but a specification is given for an "ideal" source matching the ultraviolet content of daylight. If this were fulfilled, the conditions would be similar to those sought by Hisdal and Harrison.

Grum and Wightman[17], in their study of papers containing fluorescent brightening agents, used a single tungsten filament lamp at 3000°K giving the spectral-energy curve shown in Fig. 8, apparently without filters or additional ultraviolet radiation. We must therefore add this to our list of illuminants, although it is bound to be deficient in ultraviolet compared to daylight. Such a source is the obvious choice when colours are measured that are to be seen in artificial (tungsten) lighting.

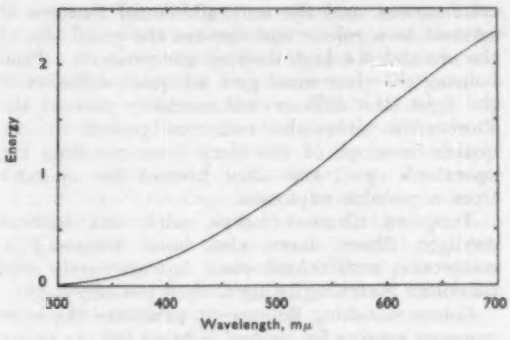

FIG. 8—Spectral-energy curve of 3000°K black-body radiator

The source used in many colorimeters, a tungsten lamp with a Chance OB8 filter, is far from lacking ultraviolet radiation [13], as shown in Fig. 9, and there will be an appreciable contribution to a fluorescent colour by the ultraviolet-excited radiation under such a source.

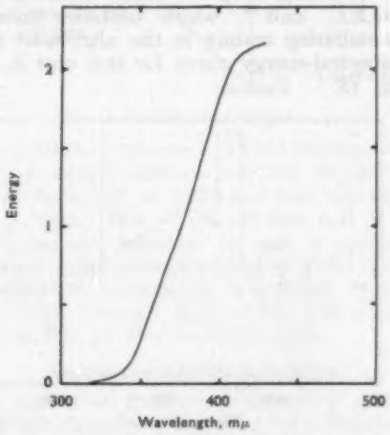

FIG. 9—Spectral-energy curve of tungsten lamp at 3000°K with Chance OB8 filter

Near-white Materials

We must separate at this point the methods of colour measurement which comply with the conditions given earlier in this paper and so are applicable to all fluorescent colours, from those techniques which have been designed specifically for the assessment of fluorescently brightened near-whites in which all the fluorescence can be assumed to be excited by ultraviolet radiation. In the former class are a suitably filtered xenon arc or Hisdal's or Harrison's source in a colorimeter or spectrophotometer in which the sample is illuminated directly by the source, and also Allen's method, provided that the "ideal" fluorimeter is used and that the colorimeter or spectrophotometer is fitted with illuminant C (with no ultraviolet content) illuminating the sample directly.

However, Allen's paper is mainly concerned with measurements of the whitening effect of a fluorescent brightening agent, and this is obviously applicable to near-whites only. Grum and Wightman's paper includes a mathematical method of separating the component of the colour that is due to ultraviolet-excited fluorescence, and this also is intended to apply only to near-whites.

Hunter's reflectometer [18] uses a single tungsten lamp as illuminant, and a movable ultraviolet filter that can be in either the incident or the reflected beam allows the fluorescence excited by ultraviolet radiation to be separated from the total radiation from the sample. Measurements of fluorescent materials with this instrument would have to be interpreted with care, as the correction of the source from tungsten-filament lighting to illuminant C is made by filters between the sample and the photocell. This means that colour measurements of fluorescent materials and of the ultraviolet-excited fluorescence are made under somewhat arbitrary conditions. In fact, although this instrument fulfils the conditions (adequate for non-fluorescent materials) that the product of the source, filter, and receptor spectral distributions must fulfil CIE specifications, it does not fulfil the condition for fluorescent materials that the source and filter/photocell spectral distributions must be specified separately.

Comparison of Methods

There has been little theoretical or experimental work comparing the results given by these different illuminants. A comparison has been made [14] between a Harrison colorimeter and the Sheen abridged spectrophotometer fitted with the source shown in Fig. 5, and this is shown in Fig. 10 and 11. In both instruments the measurements were made with a source somewhat lacking in ultraviolet (3000°K lamp with Chance OB8 filter in the Harrison colorimeter and an unfiltered tungsten lamp in the Sheen instrument), and then with the respective approximations to daylight. As expected, both instruments show the increased blueness of the near-white papers and the increased luminance and green content of the yellow and, also as expected, the change is shown as much

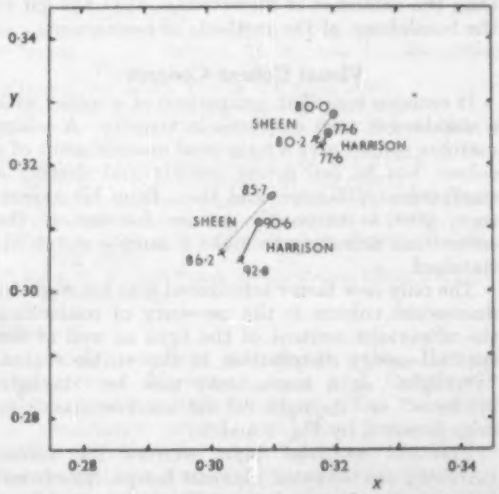

FIG. 10—CIE co-ordinates of near-whites under sources deficient in ultraviolet (○) and under artificial daylight (×)

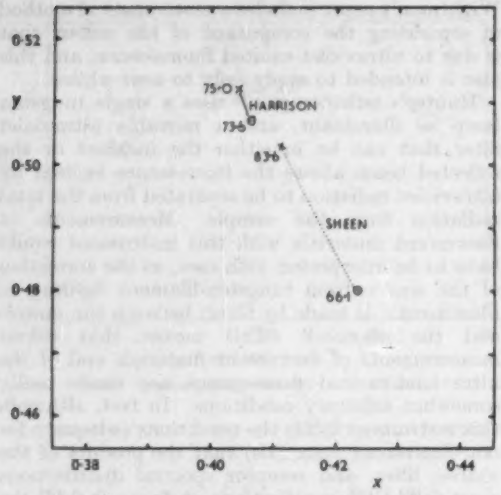

FIG. 11—CIE co-ordinates of fluorescent yellow ink under sources deficient in ultraviolet (○) and under artificial daylight (×)

greater by the Sheen instrument than by the Harrison; the difference in ultraviolet content between the two sources is smaller in the latter instrument.

Some of the references listed[6,15–17] include correlations of measurements with visual assessment of near-whites, but more work is required on the comparison of different sources and, if possible, on filters for xenon arc lamps and supplements for tungsten lamps that will make the two sources equivalent.

Friele makes the point[6] that some of the one-dimensional whiteness scales that have been developed[19] for non-fluorescent near-whites are less valid for fluorescently brightened materials, but this is not a direct consequence of the fluorescence of the latter. Fluorescent near-whites are usually bluer and lighter than it is possible to make non-fluorescent materials, and it is this increase in available colour gamut, rather than the existence of fluorescence, that has led to the breakdown of the methods of assessment.

Visual Colour Control

It remains true that comparison of a colour with a standard is most easily made visually. A colour matcher cannot give a numerical measurement of a colour, but he can detect quickly and reliably a small colour difference and then, from his experience, give a reasonably precise forecast of the corrections necessary to make a sample match his standard.

The only new factor introduced into his work by fluorescent colours is the necessity of controlling the ultraviolet content of the light as well as the spectral-energy distribution in the visible region. "Daylight" as a source may now be "daylight outdoors" or "daylight behind window glass", as demonstrated by Fig. 2 and 3.

Practical artificial light sources for colour matching are tungsten filament lamps, fluorescent tubes, and xenon arc lamps. The last-named have been discussed in connection with their use in colorimeters, and the only additional features of interest to a colour matcher are the small size of the arc and the high internal gas pressure. Their housing therefore must give adequate diffusion of the light (the diffuser will normally prevent the short-wave ultraviolet radiation passed by the quartz envelope of the lamp from reaching the operator's eyes) and must protect the operator from a possible explosion.

Tungsten filament lamps, with and without daylight filters, have also been discussed in connection with colorimeters, but are rarely used for colour matching owing to their low efficiency.

Colour-matching fluorescent tubes are the most common sources for general lighting but, as shown in Fig. 12, are somewhat deficient in ultraviolet radiation compared to daylight, and this will be true also of colour-matching units in which light-blue fluorescent tubes are combined with tungsten lamps to improve the energy distribution in the red region of the spectrum. A deliberate attempt to provide adequate ultraviolet radiation in a colour-matching lamp was made in the design of the G.E.C. unit[20], which contains fluorescent tubes radiating mainly in the ultraviolet region. The spectral-energy curve for this unit is shown in Fig. 13.

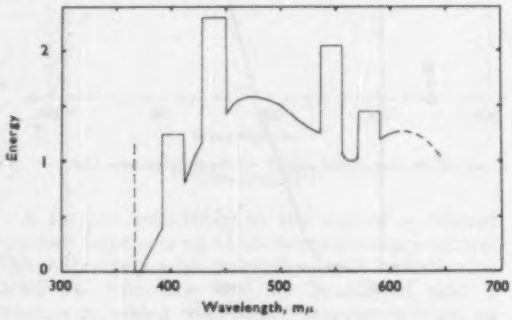

FIG. 12—Spectral-energy curve of "colour-matching" fluorescent tube

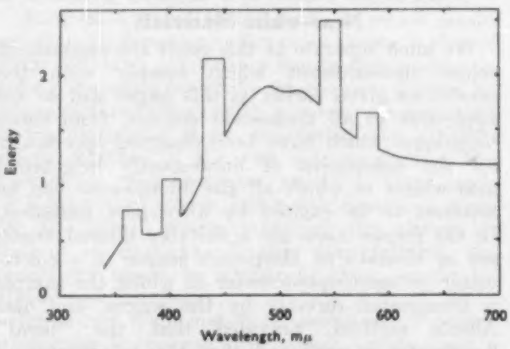

FIG. 13—Spectral-energy curve of G.E.C. colour-matching unit

Fluorimeters

A convenient practical method of measuring the effectiveness of a fluorescent material in a colour is to illuminate the colour with ultraviolet radiation (usually from a mercury lamp) and measure the visible light emitted. The layout of a typical

fluorimeter for this type of measurement is shown in Fig. 14. The mercury vapour lamp is an intense source of ultraviolet radiation and excites a considerable amount of fluorescence, so that such a fluorimeter is very sensitive. If additional colour filters are placed between the sample and the photocell, the spectral distribution of the emitted light can be estimated[14]. However, as Allen has pointed out[16], readings from a fluorimeter having a mercury lamp can only be used directly with samples containing the same fluorescent dye, and allowance must be made for different absorption characteristics if different fluorescent materials are to be compared.

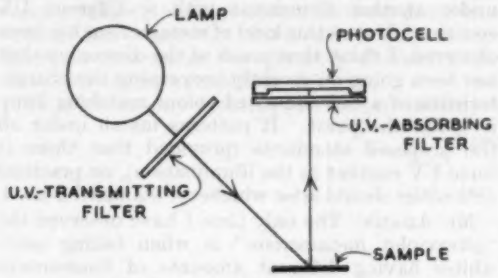

FIG. 14—Layout of fluorimeter

It is possible to operate a "visual fluorimeter" by holding a sample under a mercury vapour lamp emitting radiation at 365·5 mμ and viewing the emitted light. This is an obvious test if it is desired to see whether or not a sample is fluorescent, and it also gives an idea of the colour of the fluorescent component; for instance, the green colour under mercury light of the yellow sample shown in Fig. 11 was very noticeable.

Summary and Conclusions

The control of fluorescent colours is generally carried out visually or by means of a fluorimeter, and such methods are simple and, if used with a realisation of their limitations, adequate for maintaining the quality of a product. The main problem with visual colour control is that the colour-rendering of a light source is now a function of its near-ultraviolet content as well as of the spectral-energy distribution in the visible region. It is perhaps disturbing to consider that a match between two samples having different degrees of fluorescence may be altered by opening the window.

However, the position with regard to measurements and specifications that may have to be quoted to others is far less satisfactory. The majority of colour-measuring instruments are basically unsuitable for measurement of fluorescent colours owing to the placing of colour filters or a monochromator between the light source and the sample, and there are no accepted standards for important features of those which are designed for use with fluorescent materials. Two light sources are popular; the xenon arc is at first sight convenient but it is expensive and allowance must be made for the flicker of the arc. The supplemented tungsten lamp has the advantage that, as most of the ultraviolet component of the source is generated separately, its contribution can be varied easily, either by altering the relative intensity of the light from two lamps (as in Hisdal's method), or by altering the factor by which the supplementary measurements are multiplied before combining them with the reflectance measurements (as in Harrison's colorimeter).

As stated in the introduction, the aim of this paper is to review the methods of assessing fluorescent colours. Its main conclusions must be that practical comparisons of these methods would be useful (particularly of those methods which should theoretically give similar results), and that standards for conditions of measurement are urgently needed.

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References

1 Bouma, P. J., *Physical Aspects of Colour*, N.V. Philips Gloeilampenfabrieken (1947).
2 Harrison, V. G. W., *Proc. Phys. Soc.*, **54**, 86 (Mar 1942).
3 Kubelka, P., *J. Opt. Soc. Amer.*, **38**, 448 (1948).
4 Stenius, A. S., *ibid.*, **45**, 727 (1955).
5 Scandinavian Pulp, Paper & Board Testing Committee. *Reflectance of Paper and Paperboard: Draft Standard SCAN-P 13X* (Jan 1961).
6 Wright, W. D., *Nature*, **179**, 179 (26 Jan 1957).
7 Herrmann, R. *Optik* (Stuttgart), **2**, 384 (1947).
8 Friele, L. F. C., *Die Farbe*, **8**, 171 (Dec 1959).
9 Frühling, H. G., Münch, W., and Richter, M., *ibid.*, **5**, 41 (Sept 1956).
10 Adams, J. M., *Print. Tech.*, **3**, 3 (Jan 1960).
11 Dearth, L. R., Shillcox, W. M., and Van den Akker, J. A., *Tappi*, **43**, 230A (1960).
12 Hisdal, B., *Optica Acta*, **8**, 139 (Sept 1956).
13 Harrison, W., *J. Sci. Instrum.*, **36**, 234 (1959).
14 Adams, J. M., *Patra Printing Lab. Report*, No. 36 (Nov 1960).
15 Allen, E., *Amer. Dyestuff Rep.*, **46**, 425 (1957).
16 Allen, E., *J. Opt. Soc. Amer.*, **47**, 933 (1957).
17 Grum, F., and Wightman, T., *Tappi*, **43**, 400 (1960).
18 Hunter, R. S., *J. Opt. Soc. Amer.*, **50**, 44 (1960).
19 Adams, J. M., *Patra Printing Lab. Report.*, No. 28 (July 1959).
20 Miles, E. E., and Peach, D. C., *Trans. Illum. Eng. Soc.*, **21**, 135 (1956).

Discussion

Mr. S. M. JAECKEL: I should like to comment on another instrument in order to complete the picture drawn by Mr. Adams. He mentions the Harrison Colorimeter, and the use of its tungsten lamp light source with different filters in order to measure fluorescence as well as colour. In Fig. 14 of the paper he sketches the layout of a fluorimeter. At HATRA we have had considerable success in using another instrument, the Harrison Fluorescence Measuring Unit and Colorimeter, which combines both functions. The instrument is reasonably priced and very versatile. In addition to the colorimeter light source mentioned by the lecturer, there is a mercury discharge lamp giving mainly ultraviolet radiation, so that the instrument can readily be used as a fluorimeter.

Although the results obtained are not in absolute units, very useful numerical comparisons can quickly be obtained. The filter system also enables the relative amounts of fluorescence in several fairly wide spectral bands to be found.

Mr. Adams refers to Allen's papers on relative effective fluorescence and on the inadvisability of comparing different fluorescent brightening agents (FBA). Whilst we agree in general, there is one very rough diagnostic use of the multi-purpose Harrison instrument in which we transgress this rule. Occasionally we can tell whether similar substrates that have been treated with FBAs differ only in concentration of FBA or in type of FBA used, by measuring the ratio of blue-green to blue fluorescence for each pattern, using Harrison's filter disc. If the ratios differ markedly then it is almost certain that different FBAs have been used. On the other hand, if the ratios are similar, no definite conclusion can be drawn.

Mr. ADAMS: I have used the Harrison Fluorescence Measuring Unit, but I found that making supplementary measurements with the mercury source was impracticable owing to the time required for the lamps to warm up after changing from one source to the other. Using the relative readings of fluorescence with the different filters certainly gives a rough idea of the colour of the emitted light, but I have not had sufficient experience to distinguish fluorescent brightening agents by means of these readings.

Mr. JAECKEL: We find that fairly reliable measurements can sometimes be obtained with the mercury source after about 5 minutes, but we prefer to leave it on for not less than 1 hour to stabilise.

Dr. L. ZAKARIAS: Can Mr. Adams differentiate between bluish white and pinkish white effects on fabrics by means of present-day instruments, and can he measure the fluorescent whiteness of the fabrics? Some manufacturers warn that use of excessive amounts of fluorescent brightening agents may lead to the production of pinkish white effects. It is well known in the laundry industry that fluorescent brightening agents tend to emphasise any variations in whiteness, and in particular the "yellow centres" of white pillow-cases, which are large fatty stains not removable by established washing processes. We have deduced from large-scale experiments over the last three years that even an inexpensive fluorescent brightener will reflect continuously an excellent bluish-white colour minimising any uneven whiteness of the fabric, whatever the quantity of agent used and however often it is applied to the same white fabric, provided that the agent has been combined with a certain pretreated, water-soluble gum. Has Mr. Adams observed and can he measure quantitatively the specific protective colloid action on fluorescent brighteners?

Mr. ADAMS: The only sure way to distinguish between fluorescent brightening agents giving different colours is to illuminate them with ultra-violet radiation and to make spectrophotometric measurements of the emitted light. In general the pinkish white materials will have emission peaks in the violet region of the spectrum, whereas the bluish white will emit mainly in the blue region.

I have no knowledge of the way in which repeated applications of different fluorescent brightening agents will affect the colour of a material.

Dr. D. PATTERSON: The importance of the ultraviolet (UV) content of the light under which fluorescent patterns are viewed has been clearly brought out by Mr. Adams, but I should like to ask whether what one could call "ultraviolet metamerism" has been observed. This effect would arise if two patterns that were found to match under an illuminant that included a certain amount of UV radiation were found *not* to match under another illuminant with a different UV content. Unless this kind of metamerism has been observed, I think that much of the discussion that has been going on recently concerning the characteristics of a new standard colour-matching lamp is beside the point. If patterns match under all the proposed standards (provided that there is some UV content in the illumination), no practical difficulties should arise whichever standard is used.

Mr. ADAMS: The only time I have observed the "ultraviolet metamerism" is when taking near-whites having different amounts of fluorescence from daylight to tungsten filament lighting. I was hoping that members at the Symposium would have had experience that would enable us to judge the magnitude of the problem in practice.

Mr. JAECKEL: I should like to make an additional comment. I prefer the use of the Harrison fluorescence ratios to Mr. Adams's method of looking in a "black box" to differentiate between fluorescent brightening agents, because the ratio is a quantitative measure, so that sometimes it is only necessary to examine one pattern to be able to say whether the agent supposedly used could be the one actually used.

In reply to Dr. Zakarias, Mr. Adams has suggested the use of spectophotometric measurements to distinguish between different fluorescent brightening effects. In some instances, at least, we can differentiate more simply between "red-shade" and "green-shade" FBAs by using the tungsten lamp colorimeter light source of our Harrison instrument only: the "red-shade" whitener often yields a more violet or blue point on the chromaticity diagram.

Mr. R. J. HANNAY: With regard to the question raised by Dr. Patterson, it has been known for a long time that the use of fluorescent brightening agents on dyed textiles does give rise to alterations in the hue of the dyed material when this is viewed in lights of different UV content. This is particularly so for pale shades, and in the past has given rise to complaints about the fastness of the dyes used, although the effect is purely a visual one and is in no way connected with dye fastness.

Mr. JAECKEL: I think that two separate issues are involved in the comments by Dr. Patterson and Mr. Hannay. We at HATRA agree with Mr. Hannay that, in general, FBAs should not be used on coloured textiles, but only on whites, and even then only if the light fastness is sufficiently high.

Work at HATRA and elsewhere has shown that selected agents on selected fibres, e.g. certain specific acrylic–FBA and polyester–FBA combinations, have considerably higher light-fastness ratings than the same or other FBAs on other textile substrates. If FBAs are used with colours, they will certainly make pastel blues appear bluer and brighter, but yellows are weakened and pinks made to look grey and dirty.

With regard to Dr. Patterson's query on the effect of variations in ultraviolet content of illuminants on the appearance of FBA-treated textiles, we can make a qualitative comment of some relevance. Usually, when we examine a series of FBA-treated textiles under three light sources, namely daylight, an ultraviolet lamp in a "black box", and the fluorescence side of our Harrison instrument, we get very similar, if not identical, orders of ranking.

Dr. PATTERSON: I should like to draw attention to a paper on the Day-Glo Daylight Fluorescent Colour Specification System by R. A. Ward, published by Switzer Bros. Inc., which I think is a sound theoretical and practical approach to the problem.

Mr. ADAMS: I have not seen the paper by Ward, but there is a paper on fluorescent high-visibility paints for aircraft which refers to this and other relevant publications. It is *Fluorescent High-visibility Paints for Aircraft*, by J. S. Cowling and F. M. Noonan, *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **31** (415: Part 2) 1–19 (Aug. 1959).

Dr. A. WÜRZ*: With regard to Mr. Hannay's remarks, it may be of interest to note that we have found with certain acrylic fibres that it is possible to apply Basacryl dyes and selected fluorescent brightening agents simultaneously without seriously affecting the light fastness of the dyeing. Such a combination could be of interest, for example, in producing bright pastel colours.

* Communicated

Chairman—Mr. W. G. B. GRANT

Pigments, Colour, and Paint

S. H. BELL

Colour in paints is provided mainly by insoluble pigments, which affect many other properties. Background information is given about the nature of paint and paint films, and the essential pigment characteristics. This is followed by a description of the disposition of pigment particles within paint films in relation to coloration. Finally, colour control of pigments and colour matching of paints are discussed, and comments are made on the potentialities of instrumental aids.

General Background

In paint, coloration is in the main achieved by the use of insoluble pigments, and cannot be divorced from the effect of those pigments on other paint properties. The nature and functions of pigments can be considered only in relation to the character of paint and the tasks it has to perform.

THE NATURE OF PAINT

Paint is, in general, a fluid material easy to apply as an even coating to surfaces of wood, metal, plaster, etc., where it changes to a solid film about one thousandth of an inch thick. Some paints are used at considerably greater thicknesses, but it is usual to apply a number of coats each having its individual part to play in the complete system.

The finished work must be level, uniform in colour and texture, have a variety of other optical and mechanical characteristics (including the essential adhesion to the surface painted), and the required stability in the environment to which it is exposed. Broadly, the functions are decorative and protective. There are coatings in which transparent colour is required, but most frequently the need is for opaque coloured coatings to impose on surfaces a new colour and texture, by layers insufficiently thick to alter unduly the contours of those surfaces.

Some properties of paint are almost wholly dependent upon those of the incorporated pigments, others less so; yet others may depend predominantly upon the nature of the (usually organic) film-forming material or *medium*.

In general, the essential components of media are polymeric, or become so during the conversion from fluid to solid film. Those media which are converted to an insoluble condition include those which "dry" by an oxidation process dependent mainly upon unsaturated oily constituents, which in the course of oxidation form three-dimensional cross-linked polymeric structures containing material of lower molecular weight; the result is toughness, flexibility, and a high degree of insolubility. In other cases a preformed polymer may be deposited from solution in organic solvents or from suspension or emulsion in water. There are many possible variations, some requiring the use of catalysts or of heat to stimulate or complete the drying process.

The chemical diversity of paint types is indicated by that of the media, which may be based on or include linseed oil and a number of other drying and semi-drying oils, natural resins, and numerous synthetic resins, e.g. the alkyds (e.g. modified polymers of phthalic anhydride–glycerol), phenol–, urea–, and melamine–formaldehyde condensation products, epoxide, polyurethane, silicone, vinyl, and various hydrocarbon polymers. Other media components include nitrocellulose and other cellulose derivatives, synthetic and treated rubbers, bitumens, and tars.

PIGMENT TYPES

There are many pigment (and extender*) types, which may be classified according to origin, chemical nature, and physical form.

Naturally occurring types include certain iron oxides (e.g. C.I. Pigment Red 102, C.I. Pigment Yellow 42) and extenders such as calcium carbonate, barium sulphate (C.I. Pigment White 21, 22, and 23), diatomaceous earth, silica (C.I. Pigment White 27), and asbestine (C.I. Pigment White 26). They are processed in various ways, usually involving control of particle size by grinding in water and elutriation or selective sedimentation.

Manufactured types may be made by—

(*a*) precipitation from aqueous solution reactions, e.g. the chromate pigments, Prussian blue (C.I. Pigment Blue 27), certain iron oxide reds and yellows, and organic pigments and lakes;

(*b*) calcination, e.g. ultramarine (C.I. Pigment Blue 29);

(*c*) calcination following precipitation, e.g. chromium oxide (C.I. Pigment Green 17), zinc sulphide (C.I. Pigment White 7), and titanium dioxide (C.I. Pigment White 6) pigments; and

(*d*) smoke processes, e.g. zinc oxide (C.I. Pigment White 4) and antimonious oxide (C.I. Pigment White 11) (air oxidation of metal vapours), and carbon black (C.I. Pigment Black 6 and 7) (by combustion of natural gas and other carbon-containing materials).

There are also a number of metal pigments, notably aluminium (C.I. Pigment Metal 1), lead (C.I. Pigment Metal 4), zinc (C.I. Pigment Metal 6), and (recently) stainless steel (C.I. 77485).

Among the organic pigments the most important for paint are phthalocyanine blue (C.I. Pigment

* In the present context, extenders may be regarded as particulate materials of lower refractive index than pigments, with correspondingly smaller effects on opacity and colour, valuable in enhancing or controlling rheological, mechanical, and certain special paint properties.

Blue 15 and 16) and green (C.I. Pigment Green 7), azo yellows of the Hansa type, benzidine yellow (C.I. Pigment Yellow 12); and some azo reds, e.g. toluidine red (C.I. Pigment Red 3).

Apart from chemical constitution, the chief characteristics to be established and controlled in manufacture are crystal structure or habit, and particle size and shape, all in relation to correct colour and strength. Characteristics may be modified after the main processing by surface treatments of various kinds or by special milling processes, e.g. *micronising*. Important requirements are, in general, ease of incorporation in paint media, insolubility in water and organic solvents, fastness to light and to various chemicals, and good whiteness with high refractive index, or highly saturated colour quality.

PARTICLE SIZE AND DISTRIBUTION

The fact that a paint film is only about one thousandth of an inch thick itself indicates an upper limit of desirable pigment particle size. A relatively few oversize particles or agglomerates can spoil the surface finish. Moreover, hard aggregates of small particles difficult to break down can be troublesome in paint making.

The upper limit of coarseness is about 20 microns (μ). There is a second and lower level significant in relation to wetting and dispersion in paint making, and to the general flow, smoothness, gloss, etc. of paint films. For some purposes this may be placed at an upper limit of 5 μ (though the relative proportions of all sizes present is involved); for other purposes 1 μ may be more desirable as the predominant size.

For some pigments and paint systems there may be lower limits of particle size below which some desirable properties may be impaired. For example, at operative particle sizes below about a quarter of the wavelength of light, the opacity of white pigments is likely to be very small; for the very extensively used titanium dioxide in most organic media the optimum size is about 0·3 μ. Particle size can have profound effects on the rheological behaviour of paints. Thus, small quantities of very fine extenders can be used to adjust the degree of *body* in a system which is otherwise too slack when normal quantities of the main pigments are incorporated.

Size distribution may vary widely from pigment to pigment. The following figures are general averages of axis diameters for the predominant size range in each class—

coarse extenders	20–2 μ
fine extenders	5–1 μ
pigments of medium fineness and some of the finer extenders	1–0·2 μ
very fine pigments	0·2–0·01 μ

Shape may affect both optical and rheological properties, and general durability. Particles of true spherical shape are rare among pigments. Some are markedly needle-like or plate-like and many are irregular in shape though approximately equidimensional (see Fig. 1 and 2).

Surface areas vary considerably, some typical figures being—

Pigment type	Surface area (m^2/g) (by nitrogen adsorption)
Barium sulphate	
Blanc fixe (precipitated) (C.I. Pigment White 21)	4
Barytes (ground mineral) (C.I. Pigment White 22)	1
Zinc chrome (C.I. Pigment Yellow 36)	5
Chromium oxide (C.I. Pigment Green 17)	7
Titanium dioxide (C.I. Pigment White 6)	10
Synthetic yellow iron oxide	11
Prussian blue (C.I. Pigment Blue 27)	75
Medium carbon black (C.I. Pigment Black 7)	150
Fine carbon black	900–1000

There is much debate about the practical significance of measurements of particle size and surface area, and indeed about what is meant by a "particle". Recent high-resolution electron microscopy has revealed that, in some pigment specimens, larger units formerly considered to be single particles are in fact aggregates of very fine material (see Fig. 3). Moreover, there may be considerable differences between sizes as revealed by electron microscopy on carefully prepared specimens fully wetted and dispersed, and effective sizes in practical paint systems. This introduces questions of wettability and dispersion, and the accessibility to molecules of various sizes and kinds present in media, of surfaces within agglomerations of very fine particles or fissures in particles. Methods based on adsorption, sedimentation, and penetration of pigment masses by gases and fluids can be used to explore these factors.

OPTICAL PROPERTIES

The obliterating power of a paint depends mainly upon the amount of scattering and the absorption of light by the pigment. With whites and pale tints there is little absorption; white pigments, e.g. titanium dioxide (refractive index 2·7) and zinc sulphide (2·4), scatter strongly in organic media, many of which have refractive indices of about 1·5.

To meet the colour-control requirements of paint (which are dealt with later), pigments need to be closely reproduced in successive batches not only as to colour but also as to strength (variously called tinting strength, staining power, or colour in reduction), which is the ability to impart colour to a mixture with other pigments in a paint medium, in particular, in the making of tints in heavy dilution with white in a paint medium.

Observations are made on pastes, full colour and diluted with white, against a standard pigment (e.g. a sample from a previous batch). It is common to draw-down pastes with a palette knife so as to give wedge-shaped films running from, e.g. 50 μ to zero, in bands about 1 in. wide and 3–4 in. long. In the thinner parts the dominant undertone of the colour can be seen and in the thicker parts tendencies towards *floating* or *bronzing* (see later) may be revealed.

In making truly comparable observations on reduced colours a number of variables must be controlled. The selection of the white pigment and of the oil or other medium, the ratio of colour to white, and the method of preparing the pastes

all affect the result. This is because one coloured pigment may be more or less strong than another according to the conditions. The tinting curves for successive additions of white to two similar coloured pigments may cross, and they may cross at different levels according to the medium used to make the pastes and the pigment–medium concentration.

These various factors must be borne in mind when considering the intended use of the pigments, but a typical general test for strength is included in some B.S. pigment specifications. For example, Prussian blue (0·1 g) is rubbed out with a specified acid-refined linseed oil using a palette knife or muller on a non-absorbent slab for 5 min, and a separate paste of 5 g zinc oxide is made similarly. The total amount of oil used is "approx. 1·5 ml". The two pastes are then rubbed out together until no further colour change occurs, and "tone and intensity of colour" are compared with those of a paste made similarly, using an agreed sample. The manner of spreading out and viewing the pastes is defined.

Light-fastness is an important property, which in practice involves more than the resistance to fading or darkening of the pigment, but also the nature of the medium, which itself may alter in colour on exposure to light. Tests are therefore made on paints. A typical procedure (Specification DEF 1053, Method No. 33) is to expose a painted panel at a distance of $10 \pm 0{\cdot}25$ in. from an enclosed carbon arc running at 1·3–1·5 kw. The temperature of the air in the proximity of the panel is maintained at 38–44°C. After exposure for the specified time (72 or 168 h according to paint type) there must be "little or no change in colour" and this must not be greater than that shown by approved materials.

In recent years there has been a developing interest in the use of the blue wool standards of *BS* 1006 for assessment of light-fastness, encouraged by the Oil and Colour Chemists' Association through a co-operative investigation scheme.

OTHER PIGMENT PROPERTIES

Specifications for pigments (e.g. those of the B.S.I.) usually cover chemical composition and limits for impurities— water-soluble matter and volatile matter (usually at 98–102°C)— colour and strength, fastness to light, alkali or acid resistance, and so on, according to type. A common requirement is freedom from "coarse particles", usually by a "residue on sieve" (240 mesh) test, i.e. at a limit well above those already indicated for acceptable particle sizes.

Oil absorption is required to lie within upper and lower limits specified for each pigment. It is assessed by rubbing out the dry pigment (5–10 g according to type) with linseed oil using a palette knife under "maximum work conditions" until a coherent mass is just obtained, and determining the amount of oil required per 100 g of pigment. Oil absorption is a function of particle size and size distribution, shape, facility of particle packing, ease of wetting and dispersion by the oil with driving out of air and filling of voids by oil. Being expressed by weight it also involves specific gravity, which is widely variable among pigments. Typical figures are—

	Specific gravity	Oil absorption
Red lead (C.I. Pigment Red 105)	6·8	4–10
Lead chromes (various grades)	5–7	8–40
Red iron oxides (natural)	4–5	8–20
Ultramarine	2·4	30–40

Determination of oil absorption is a much criticised test, and for some purposes more useful results can be obtained from paste-making experiments with the medium to be used in the paint, at pigment to medium ratios nearer to those for practical paint milling. Sometimes the results are expressed by volume, and for many pigment–medium systems certain paint properties change markedly at critical pigment volume ratios typical of each system.

In spite of the wide range of specification and other tests, pigments are not thereby fully characterised. In selecting and judging pigments, the paint maker must rely for the rest upon technical experience of behaviour in paint milling, in the formation of paint films, and the effects of pigments on film properties. The operative conditions may be briefly summarised as follows.

The pigment as received by the paint manufacturer should be capable of being wetted and dispersed by the medium (which may be one of many types) to a satisfactory operative particle size range. During milling in paint making, the pigment is "opened up" so that the particle surfaces become accessible to the medium (wetting) and then, through the establishment of an adsorption or reaction condition at the interface, the particles remain separated when work ceases to be done by the mill (dispersion).

The product must display good storage stability; heavy settlement is to be avoided, particularly any tendency towards the formation of tightly packed sediment difficult to redisperse by stirring. Freedom from colour change due to chemical or physical changes in the pigment is important (see Fig. 4).

The product must maintain the consistency appropriate to its intended mode of application to surfaces, or be capable of being brought to that condition by stirring or by the addition of a diluent, as appropriate, all without unduly disturbing the desired state of pigment dispersion. The rate of shear involved in light stirring, pouring, general handling, etc. at this stage is in the region of 10–100 s^{-1}. Application may be by brush, spray, roller, dipping, and so on. The forces involved can be very large and may affect the state of dispersion. Under a brush, for example, paint is subjected to rates of shear in the region of 5,000–10,000 s^{-1}, or even higher.

There must then be good flow of the wet film to a level finish obliterating brush or other marks typical of the application method, but not so much as to cause *runs* or *sags* in the coating. This implies the correct reaction to a very low rate of shear (approx. 0·1–10 s^{-1}) in which surface tension forces take part. In other cases the

rheological condition must be such as to provide special texture effects.

Then the film dries, and the pigment and its disposition within the film must be such as not to interfere with, but rather to assist, the drying and the development of hardness, toughness, and flexibility as required and, of course, good adhesion. The optical properties (gloss, mattness or other finish, colour, and opacity) should be fully established at this stage.

In the period of film drying there is a fundamental change in condition, from fluid to solid; moreover, in many cases the medium changes chemically. During the change there is considerable mechanical disturbance within the film, with evaporation of solvent, concurrent volume changes, etc.

Even in the dried film, polymerisation with hardening and slow loss of residual solvent may occur, leading to general ageing and finally to breakdown. These changes are in general accelerated by light (and particularly by ultra-violet radiation), moisture, temperature variations, and atmospheric factors generally, including atmospheric pollution and various other chemical or physical influences in particular exposure environments.

Coloration and Pigment Distribution in Paint Films

The foregoing discussion emphasises the fact that the pigment–paint relationship is basically different from the dye–fibre relationship in that the pigments used are an essential part of the structure of paint films and affect many properties besides colour.

Paints of different colours cannot in many cases be made by simply changing the pigments, without further adjustment. Different pigments have different chemical compositions and different interactions (physical and chemical) with paint media. There are a few chemical types which provide a wide range of colours dependent upon variations in chemical composition within the species, in crystal structure, or in physical form. For example, in the iron oxide range, pigments are available from yellow, through reds and brown, to black. Similarly, the chromate range covers pale green–yellows, through the yellows, to orange–reds. In many other cases the variation within each group is small.

The choice frequently depends more upon the chemical nature of the pigment relative to the intended use and exposure environment of the paint, e.g. whether it is likely to meet acid atmospheres, alkaline substrates, etc. Other chemical factors affecting choice include interference with the drying reactions of the organic medium, particularly when the paint is used after long periods of storage, or a tendency to react with acid substances in the medium to form soaps such as might affect storage stability. Where, however, the development of properties associated with a particular pigment is sought, the nature of that pigment determines the choice of medium. Anti-corrosive primers provide good examples. Red lead, various chromates, and calcium plumbate are among those pigments which require careful choice of medium if their specific chemical or electrochemical anti-corrosive functions on various metals are to be achieved.

However, in returning specifically to coloration, and leaving aside chemical relationships between pigment and medium, it is valuable to consider the distribution of pigment particles in a paint film and some of the complicating physical factors.

PIGMENT CONCENTRATION

There are paints in which the coloured pigment, or a mixture of pigments, provides a very large part of the pigment component; there are many others in which the dominant pigment component is a finely divided opaque white, e.g. titanium dioxide, with coloured pigments as tinters.

In a typical case, e.g. an ordinary gloss paint based on an alkyd medium, there would be about 45% white pigment by weight or 17% by volume. In a pastel shade there would be, e.g., white 42% and coloured 3% by weight, or approx. 15% and 2% by volume. Assuming particle diameters of the order of 0·25 μ and full dispersion and separation, the distances between the particles would be approx. 0·55 μ, though in practice a uniform array is seldom achieved (see Fig. 5). For a paint film 25 μ thick, one cm^2 would contain about $5{\cdot}5 \times 10^{10}$ particles, and the surface area of the particles in contact with the medium would be about 100 cm^2. For matt paints these pigment population figures can be trebled and the pigment becomes an even greater factor in determining film structure and properties.

These data are significant in terms of physico-chemical effects, and also in relation to opacity and colour via light scattering and adsorption.

OPTICAL EFFECTS

When light strikes a paint film, some (usually about 4% for normal incidence, depending on the refractive index of the medium) is reflected externally without entering the film. The light which actually enters the paint film strikes the pigment particles, which absorb some and scatter the remainder. With a very thin or inadequately pigmented paint film, some of the light may pass through the film, but for a paint film of *hiding thickness* (sufficient to hide completely the substrate to which it has been applied), all of the light is either absorbed by the pigment or scattered back as diffusely reflected light. Ignoring certain complications which result from the internal reflection of this scattered light at the medium–air interface, the proportion of the incident light of any one wavelength thus reflected is equal to the measured reflectance, R, and is related to the coefficients of absorption (α) and scatter (δ) of the pigments by the familiar equation $\theta = \alpha/\delta$, where $\theta = (1-R)^2/2R$.

The values of α and δ for a particular pigment vary with its particle size and the refractive index of the medium. The coefficient of absorption (which is different from the extinction coefficient of the substance in large crystals) rises continuously as the particle size is decreased, but the coefficient of scatter for a given wavelength passes

through a maximum at a certain particle size. In the case of white pigments, where their hiding power depends almost entirely on the scattering, there being little absorption, it is clearly important that the particle size should be close to that giving maximum scatter. Change in the refractive index of the medium affects mainly the value of δ, which falls to zero if the refractive index of the medium is the same as that of the pigment.

Black pigments have a high coefficient of absorption at all wavelengths and a low coefficient of scatter. Brightly coloured pigments have low absorption and high scatter in the region of the spectrum corresponding to their colour, and high absorption in other regions. Many coloured pigments (e.g. Prussian blue, ultramarine, and many organic pigments) lack high scatter in their region of low absorption and, consequently, when used as sole pigment in a paint, produce a dark colour and lack opacity. This can be remedied by adding a white pigment, which supplies the necessary scatter.

The coefficients of scatter and of absorption of a paint containing a mixture of pigments are simple additive functions of those of its component pigments, provided that the pigments are adequately dispersed and evenly disposed so that the optical properties (colour, hiding power, etc.) can be predicted quantitatively. The general expression from which the reflectance at each wavelength, and hence the colour, may be calculated is

$$\theta = (C_A\alpha_A + C_B\alpha_B + \ldots)/(C_A\delta_A + C_B\delta_B + \ldots)$$

where C_A, C_B, etc. are the concentrations of the pigments A, B, etc., conveniently expressed as the percentage by weight of the total pigment. For a pale tint composed mainly of a white pigment, W, this approximates closely to

$$\theta = (C_A\alpha_A + C_B\alpha_B + \ldots)/100\delta_W .$$

For such paints, θ is thus a simple additive function of the coefficients of absorption of the pigments present.

PIGMENT FLOTATION

In utilising these principles to forecast what paint film colour is to be expected from various pigments in admixture, or in connection with colour control and matching (see later), complexities arise not only from the difficulty of reproducing exactly the general dispersion of particles within the medium, but also from any special distributions of particles. One such derives from pigment flotation.

The place at which any individual particle comes to rest in the film depends on several factors, including concentration; the case of a matt film of high pigment content is manifestly different from that of a glossy film containing relatively little pigment. If, however, there is room for the pigment to move, there will be a dependence on density, pigment particle or aggregate size and shape, wetting and dispersion, surface tension, and so on.

These various factors operate in a given medium to different relative extents for different pigments, which therefore may take up different positions of rest at different levels in dried films containing them in admixture. This can occur in white paints but is most obvious in coloured paints, because the surface may then become of a different colour from that underneath. The appearance is as of one colour coming to the top—hence *floating* or *flotation*. Common manifestations occur with mixtures of very finely divided pigments (e.g. Prussian blue and carbon black) and coarser pigments of higher density. The finer pigments consist, at least in part, of particles so small as to form a colloidal suspension in the medium carrying the colour in the floating and normally transparent surface layer of a glossy paint film. With such paints colour differences between top and underside will be clearly revealed on examining a painted glass panel. Moreover, flotation is usually greater in thick than in thin films, so that across a painted surface colour may vary with variations in thickness.

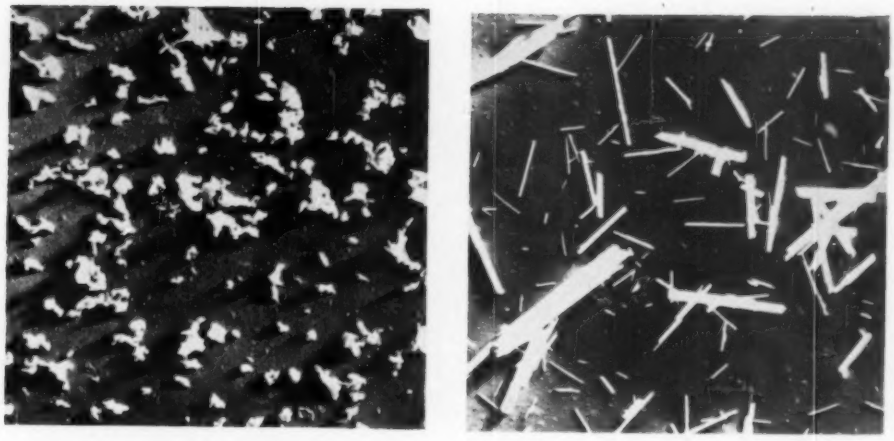
Careful attention to choice of pigment grades, the composition of the medium, and paint milling techniques, and the use of special agents are the means for overcoming the defect, but stubborn cases remain and more investigation of mechanism and control is needed.

The same is true of a particular form, sometimes called *mottled* or *cellular* flotation or *Bénard cell formation*, the last after the French investigator who in 1901 described the cellular phenomena in fluid layers. Similar patterns have been observed in cloud formations, in smoke layers, in gas formations on the sun's surface, and in films of lubricating oils and of waxes.

Simple cases are provided by fluid layers receiving heat from below and losing it above. As density is dependent on temperature, there is in such systems also a density gradient—initially, higher density above and lower density below, so that the system is unstable, the upper portion tending to sink and the lower portion to rise. In such circumstances, and with no other disturbances, a circulation (convection) cell system is developed, and in the ideal case each cell has a regular hexagonal cross-section. Frequently the upward current is in the centre, the downward current being down the edges, though in certain circumstances the reverse may be the case. In practice there may be irregular hexagons, pentagons, and so on, but the cellular pattern is typical and easily recognised. During its formation there is considerable movement within the convection cells.

In a drying paint film, the situation is analogous, though more complex. There are changes in density as solvent or other volatile material is lost, in surface tension, and in viscosity. The precise roles of the various factors are not fully understood, but the net result is a cellular pattern of unit size 2–3 mm or smaller (see Fig. 6*b*).

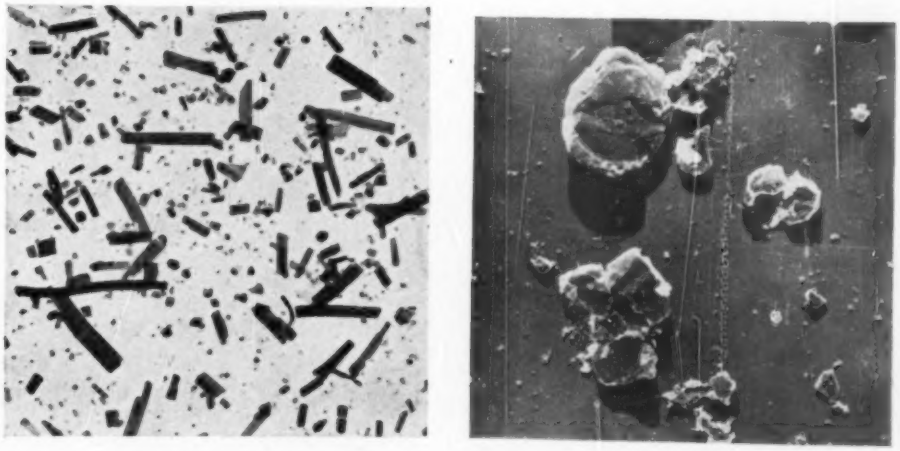
The fine mottled effect is three-dimensional by reason of humping at the centre of each cell unit, and is most evident in coloured paints containing mixtures of pigments which differ markedly in particle size or in some relevant dispersion



(a) (b)

(a) Benzidine yellow (C.I. Pigment Yellow 12), × 10,000
(b) Lemon chrome (C.I. Pigment Yellow 34), × 5,000

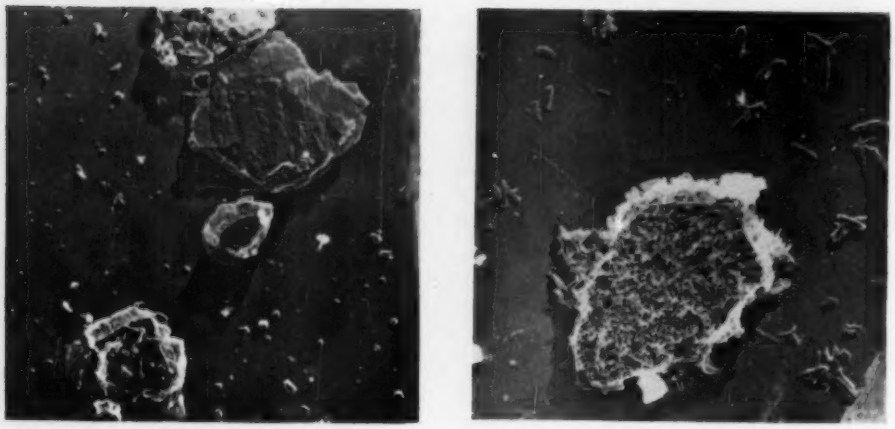
FIG. 1— Electron micrographs (metal-shadowed specimens)



(a) (b)

(a) Lithol toner (C.I. Pigment Red 49): direct transmission, × 6250
(b) Ultramarine (C.I. Pigment Blue 29): carbon-shadowed replica showing surface texture of particles, × 3000

FIG. 2— Electron micrographs

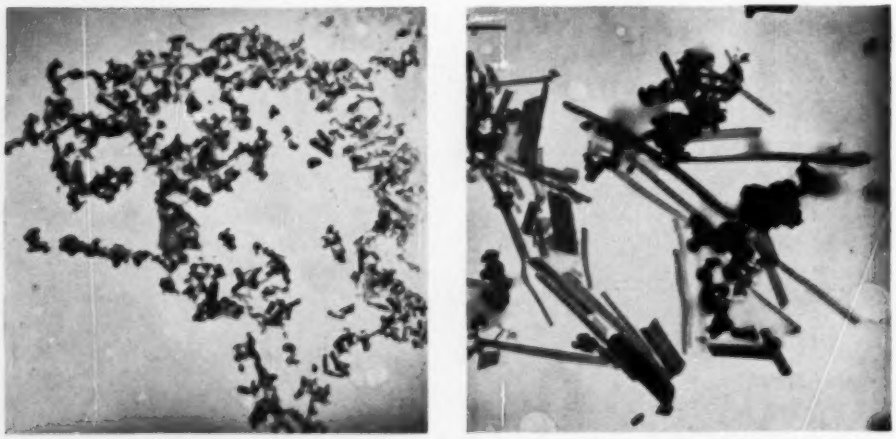


(*a*) (*b*)

(*a*) Ultramarine, single large particles, × 5600

(*b*) Yellow iron oxide, a "large particle" revealed as an agglomerate of numerous very small particles, × 5600

FIG. 3— Electron micrographs (carbon-shadowed replicas)



(*a*) (*b*)

(*a*) PVA emulsion paint with Hansa-yellow-type pigment and titanium dioxide, freshly prepared and showing full development of colour, × 6250

(*b*) As (*a*) after storage during which the colour was much reduced owing to conversion of the yellow pigment from fine particles to large crystals, × 6250. The change is prevented by correct medium formulation

FIG. 4— Electron micrographs of polyvinyl acetate (PVA) emulsion paint

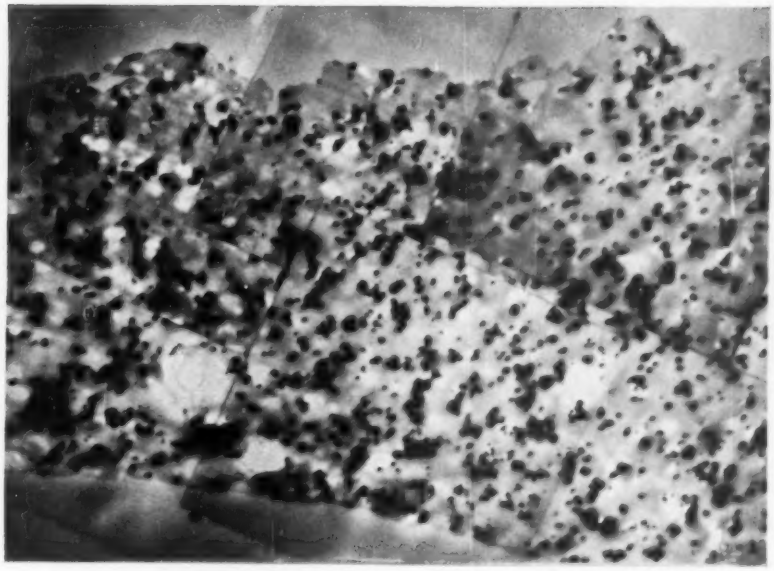
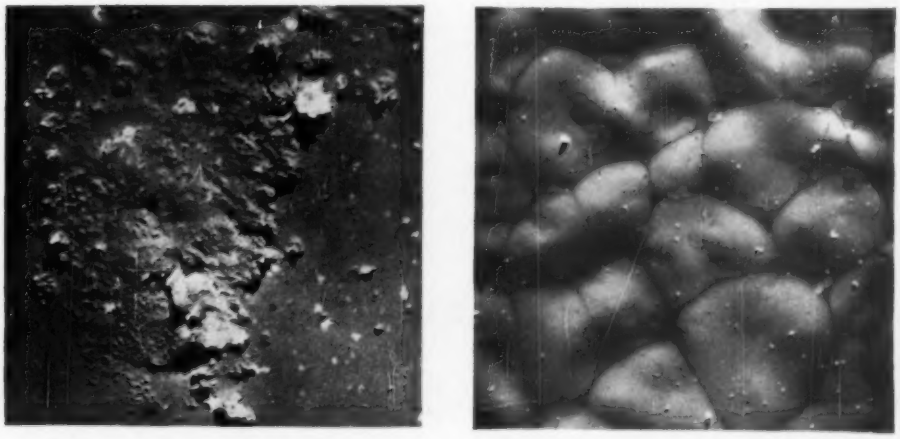


FIG. 5— Electron micrograph of section of paint film. Direct transmission through thin section taken vertically through the film. Mosaic of six micrographs covering the lower two-thirds of the film thickness, × 2500



(a) (b)

(a) Electron micrograph (surface replica) of bronzing film showing a "raft" of fine particles above the general surface level, × 6250
(b) Optical micrograph of film showing Bénard cell formation, × 12

FIG. 6

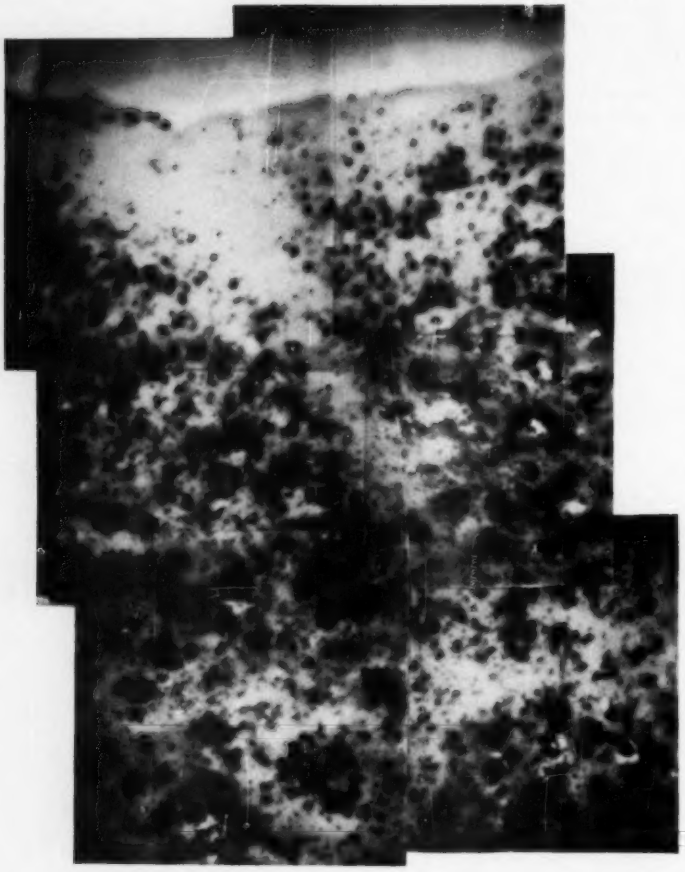


FIG. 7— Electron micrograph of section of paint film. Direct transmission of vertical section. Mosaic of six micrographs— showing Bénard cell formation in depth, ×2000. The slight depression in the surface with the funnel of relatively clear medium going down into the film corresponds to the boundary between adjacent cells

characteristic. Moreover, there may be secondary patterns and variations according to the plane in which the film dried, whether horizontal or vertical, the patterns being elongated in the latter case.

An important feature is that cells which produce the surface effect go deep into the film, giving vertical planes and lines differing in mechanical properties from those of the body of the material (see Fig. 7). This can affect subsequent performance when embrittlement becomes a precursor of breakdown. Such has been observed in a white paint in which the cell formation was not suspected (there being no colour differentiation) until after a period of weathering, when the Bénard pattern became apparent in small cracks interspersing larger cracks typical of breakdown.

The effect of cell formation on mechanical properties may be beneficial, for it may release strains easily and fairly regularly throughout the film on ageing—in some systems a valuable alternative to sudden release with the formation of large cracks and fissures.

From a coloration point of view, however, cellular flotation is a troublesome defect. Control calls for careful attention to formulation.

BRONZING

Bronzing provides another example of heterogeneity of pigment disposition in a paint film. It is due to the floating of very fine particles of pigment on, rather than in, the surface in the form of *rafts* having characteristic reflectance (see Fig. 6*a*). The thickness of the rafts deduced from shadowed electron micrographs is approx. 0·5–1 μ. The effect may occur immediately the film is laid down, or it may develop only on weathering, as medium is degraded and disappears. The degree of bronzing is inversely dependent on the wetting power of the medium; a good wetting medium keeps the pigment within the film. By choice of medium, bronzing may be suppressed or enhanced, but control is by no means absolute, and primarily it is a matter of selection of appropriate pigments.

Some highly coloured pigments have strong absorption bands in particular spectral regions, absorption being complete just inside the pigment surface. The energy thus taken up is re-emitted as light of similar wavelength. The net effect is a selective reflection of the same kind as occurs at metallic surfaces; white incident light on ordinary glossy paint films, whatever their colour, produces white highlights; on metals it produces highlights of the same colour as the metal.

Pigment particles floating on a film and substantially free of medium are in the right condition to give these optical responses, and their fineness enhances the metallic effect by the near planeness of the surfaces of the rafts. Coarse irregular particles similarly placed would provide less mirror-like layers.

Bronzing pigments give interesting effects on dilution with white pigments, with the interplay between their production of colour, by the normal absorption processes as well as by selective reflection, and the high scattering power introduced by additional white pigment.

Plotted on a trichromatic (chromaticity) diagram the path from full colour to white at the centre is circuitous. Few pigments on dilution with white pigment give a straight path on such a diagram, but the departure from straightness for bronzing pigments can be very marked. Additions of white may at first strengthen the colour, further additions change the hue, and yet further additions weaken the colour progressively to white or neutral. There may be a variety of effects.

In a particular example, a bronzing Prussian blue which in full colour had a brilliant red bronze showed steady reduction in intensity of colour with addition of barium sulphate until at 40% coloured pigment in the mix there was a sharp change in hue; thence progressive loss of red occurred but without loss of colour strength up to 10% coloured pigment. Finally, on further dilution with white the material behaved like a normal blue pigment.

Colour measurements on such systems can be made with light at the specular angle to give the bronze, under diffuse conditions to give an overall effect, or in dilution with white beyond the level critical for each pigment (as illustrated above) to give the basic colour or undertone.

Colour Control

PIGMENT COLOUR CONTROL

The same control of chemical and physical factors is necessary in the production of pigments as for many other chemical products. Control of particle characteristics is, however, a matter of major importance. There are size limitations which are set by the mere fact that the products are to be used in paint, as has already been shown, and there are direct effects of particle size on colour, strength, and undertone. Two examples of investigations of these effects will be described.

Samples of hydrated iron oxide were taken at stages in the production of a single batch. They ranged from the original first-formed particles to sizes representative of the normal pigment and beyond. Studies were made of crystal structure (X-ray analysis), chemical composition, surface area (nitrogen adsorption), particle size and shape (electron microscopy), and optical characteristics (scatter, absorption, reflectance) at full strength and on dilution with white pigments in various media.

All samples were of similar acicular particle shape and similar crystal structure, all being α-FeOOH (goethite) and closely corresponding to $Fe_2O_3.H_2O$. Size was the main variable, the size range being ten-fold. Samples having the smallest particles (surface area approx. 65 m^2/g) were brown and lacked opacity, but they had high tinting strength and gave clean yellow tints on dilution with white pigment. In the middle range, typical of normal commercial materials (about 10–20 m^2/g), the colour was yellow–orange, the opacity was higher, and the tinting strength only slightly lower. The tints were clean and of a good yellow. The samples in which the particles had been grown (to about 6 m^2/g) to exceed in size those of normal commercial hydrated iron oxides were more

orange, the tinting strength was low, and the tints on dilution with white were redder than the others.

These changes in colour properties are to be expected from fundamental physical principles. The particles of the first sample had a diameter considerably less than the wavelength of light, being therefore unable to scatter light efficiently, although, owing to their smaller size, they had a higher coefficient of absorption than the larger particles. Low scattering and relatively high absorption means that little light is scattered back by the pigment particles, and the colour is dark unless a white pigment is added to provide the necessary scatter. The colour of the tints is a clean yellow, since the blue absorption band is at its greatest intensity for the smallest particles.

As the particles grow, a point is reached where they are of the right size to have maximum scattering for short-wave violet light. As they increase in size, it seems that the maximum scattering for longer wavelengths is reached and the largest particles have the highest coefficient of scatter for red light, whereas that for shorter wavelengths is falling again. This naturally leads to a brightening and, at the larger sizes, a reddening of the colour, which is further contributed to by the weakening of the absorption band to which the yellow colour is due.

Another example comes from among pigments that are calcined in production. Samples of chromium oxide green (C.I. Pigment Green 17) were made in the laboratory from a primary sodium chromate (wet) reduction product, portions of which were then calcined in air at successively higher temperatures. Somewhat similar physical and chemical studies were made as for the iron oxides. The results were as follows—

Calcined at (°C)	Average particle diameter (μ)	Colour	Tinting strength	Notes
600	0·1	Dark green	Poor	Particles irregularly shaped
700	0·2	Brighter green	Fairly high	
920	0·5	Bright yellowish green	High	Tints have a yellowish undertone
1000–1050	1·0	Dark bluish green	Poor	Tints have a bluish undertone Particles are hexagonal and plate-like

X-ray analysis gave the same absorption lines for all samples, but sharpness and intensity differed. The increasing sharpness was attributed to increasing crystallite sizes. The differences in relative line intensities were small, but suggested that minor structural defects were progressively removed as the crystallites increased in size. The electron micrographs suggested that the particles in the samples calcined at the lower temperatures were very imperfectly formed, whereas those calcined at higher temperatures were progressively less imperfect.

The coefficient of scatter changed with particle size in the manner expected theoretically. Scatter vs. wavelength curves had maxima at the long-wave edges of the absorption bands, and the actual value of the coefficient of scatter at any particular wavelength increased with particle size, up to a diameter of about 0·2–0·5 μ. The particle size of the sample calcined at 1000–1050°C was evidently well above the optimum for scattering of visible light and there was very low scatter at all wavelengths in the visible, scatter increasing in the longer-wave infrared region.

The absorption bands became sharper and more intense as the temperature of calcining increased to 920°C. This is probably an effect of the greater perfection of crystal structure; change in particle size alone would produce a change in the opposite direction. The larger particle size of the sample calcined at 1000–1050°C was, however, consistent with the expected drop in sharpness and intensity of absorption.

These examples indicate the dependence of colour on particle size, but in many cases crystal structure and the presence of impurities, non-stoichiometry, and other physical factors, e.g. particle shape and the distribution of shape and size, can have important effects.

PAINT COLOUR MATCHING

The standard of matching of paint colours is very high, a good deal higher than in industries where the nature of the product sets a limit to the closeness of matching or where the circumstances of use are less critical. The importance of colour reproducibility is exemplified by the need to avoid obvious colour differences (*a*) between adjacent wall areas painted with different batches of the same paint; (*b*) between parts of consumer durables which may later be assembled, or in retouching or patching damaged areas; and (*c*) in "expanding" systems of, for example, metal furniture to which units may be added at different times. Colour matching is a highly skilled occupation, requiring critical judgment of small colour differences, detailed experience of the colour effects of various pigments, and ability to embrace complicating factors, e.g. different surface textures, gloss, mattness.

Reproduction of batch colours calls for suitable master and working standards (colour patterns), comparisons being made on samples not less than 3–4 in. square; larger areas (up to a foot or so square) are recommended for very close matching. Sample and standard should be held in the same plane, and should touch on as long a contact line as possible, to avoid edge effects, and it is advantageous to view both sample and standard on a background of approximately the same colour.

Good lighting conditions are essential. Good daylight is ideal, but if it is necessary to use artificial lighting, the most suitable available at present is based on carefully chosen fluorescent lamps, sometimes with tungsten lamps to supply more energy at the red end of the spectrum, in

which some fluorescent lamps are deficient. The xenon arc lamps now becoming available give an intense white light, with high emission at all wavelengths of the spectrum, and it is likely that eventually they will become more widely used for colour matching. Whatever type of artificial light is used, a final check should be made in daylight.

The colour matcher should have normal colour vision, for which a number of tests are available, notably the Ishihara charts. It is also desirable that his power of colour discrimination be high; this can be tested by the colour aptitude test developed by a committee of the U.S. Inter-Society Color Council.

The matching problem is complicated by the fact that the colour adjustment of the batch to meet the required match in the dried film has necessarily to be done on the fluid, and colour changes may occur during drying. At least, the *texture* of a wet film is different from that of a dried film and affects judgment of colour, although an experienced colour matcher can allow for likely differences between wet and dry films. Sometimes wet standards are used (e.g. samples of previously accepted batches); final matching is, however, often carried out on films dried rapidly, e.g. by mild stoving, or by full stoving for industrial finishes of the stoved type.

The question arises: Why cannot an exact formulation be used in making the paint so that there is no need for final colour adjustment? The answer lies in uncontrolled variations in pigment dispersion from causes not yet adequately defined, and subtle variations in component materials.

Care is taken in many cases to under-tint rather than over-tint in the primary formulae so that, e.g. in a pastel shade, small additions of colour can be made, rather than very large additions of white, which would unduly increase the quantity of paint required.

In some cases special needs may be met by tinting with colour pastes, each containing a single pigment, a standard white paste in the required medium. In this connection, there have been major developments in the last few years of unit tinting schemes for the retail sale of paint. The purchaser chooses his colour from an extensive range of colour patterns, and a code against that colour indicates the tinters and the quantities of them required to be added to a base paint (usually white) either by automatic dispenser or from unit tubes. Such schemes call for accurate reproduction of tinters in colour, strength, and dispersibility.

In normal factory procedures for colour matching, passage from the mill batch to the finished product usually involves from two to six adjustments before matching to standard is achieved. Some of the ways that are being developed to reduce the time so consumed will be described later.

TOLERANCES IN MATCHING

A basic requirement of instrumental methods either for recording colours or as an operational aid is that they shall be capable of dealing with small colour differences of importance in paint matching, i.e. with commercially acceptable visual differences. In determining the magnitude of such differences, investigations have been made in which colour matchers, instruments, and series of near-match painted panels played a part.

In one experiment 20 colour matchers were each given a standard painted panel (a "light biscuit", *BS* 381C) and 24 near-match panels tinted away from the standard in various directions by small progressive additions of red, yellow, green, blue, black, or white tinting pastes. The steps were chosen so that the furthest panels in each set would, it was judged, be sufficiently far from the standard to be rejected fairly consistently as commercial matches, while most of the nearer panels were considered likely to be acceptable to some observers but not to others. The aim was to provide material for statistical appraisal of acceptability.

The observers were asked to compare the panels with the standard, one at a time and in a given (random) order, and to accept only those suitably close to the standard for routine production of a high-quality stoving finish. There were fairly wide variations among the observers, particularly where individuals were normally concerned with other types of paint products, but the majority gave 6–8 of the 24 panels as acceptable matches to the standard.

Comments on the panels were confined in the main to (*a*) very simple terms such as "too yellow", "too red", "too green" or their opposites, implying that the hue required correction, and (*b*) terms more difficult to interpret, e.g. "too pale", "too deep", "too dirty", "too clean". Terms such as "warmer", "richer", "brighter", and "fuller" were used only in a few isolated cases. Although most of the comments were of this descriptive character, some observers indicated what was needed to put the colour right, e.g. "more red", "more white", etc.

An extensive analysis was made of the results which, when considered against instrumental measurements of the panels using a Beckman photoelectric spectrophotometer, indicated that samples with a colour difference less than 0·25 N.B.S. units* were sometimes rejected, though there was evidence that even smaller differences were detectable. The average level of acceptance by 50% of observers was 0·25 N.B.S. units in any colour direction, with up to nearly 1 N.B.S. unit in certain preferred directions.

In further experiments, panels were prepared from paints provided by manufacturers, either (*a*) from successive batches (in one case 50 batches made over a period of a year) and all accepted as commercial matches to a standard for the particular types of production and end-uses, or (*b*) in small groups with information as to whether or not these colours had been considered acceptable. Some were general decorative finishes and others

* The N.B.S. (National Bureau of Standards) unit combines the expression of colour quality difference on a uniform chromaticity diagram with a lightness scale based on the square root of the luminance factor, the magnitude of the unit being chosen to be five times the smallest difference that a good observer can see and such that differences of less than one unit would be unimportant "in most commercial transactions".

The eye of an experienced observer can, in fact, discriminate surface colours, e.g. between painted surfaces of similar texture, down to 0·2 N.B.S. units or even less.

industrial stoving finishes requiring very close matching. It was found that, for the latter, tolerances of only about 0·5 N.B.S. units were allowable in a white and in a grey–green series, with up to 0·75 for light blue and light green, which were the other subjects. The luminance factor tolerance was in all cases no more than 5·5% of the figure for the standard. For some decorative finishes the figures were higher, namely 1·0 N.B.S. unit for a cream, an ivory, and a "vellum", and 2·0 for a green, but with some admissions rather higher, particularly in a series in which the samples represented a large number of repeat batches over a long period.

Recent observations suggest even closer control and emphasise that a very high level of discrimination must be achieved by instrumental aids.

COLOUR MEASUREMENT

The first main purpose for which colour measurements may be required in paint technology is to provide an absolute basis for colour standards, independent of the well-known instabilities of material standards. For this purpose photoelectric spectrophotometers designed for dealing with reflecting materials are most suitable. These instruments include, on the one hand, the relatively inexpensive manually operated types, e.g. the Unicam, Uvispek, and Beckman DU instruments, and on the other hand the more expensive but highly convenient recording types, e.g. the GE (Hardy), Beckman DK 2, and the Perkin Elmer instruments.

The spectral reflection curve which these instruments give is usually recognisable in general terms as representing colour of a certain type, but is not usually interpreted in detail in terms of the colour without further calculation (using the colour response data of the eye) by which the results are translated into a trichromatic system such as the CIE system. The reflection curve itself provides more information about the sample than just its colour. The shape of the curve can frequently be used to give some indication of the types of pigment used to produce the sample and, perhaps more important, it enables a sample to be matched in spectral distribution as well as in colour, thus ensuring that the match will remain good under any conditions of illumination.

The second main purpose is to assist colour control in a number of possible ways which are discussed later. Here, three-filter photoelectric comparators give a rapid and precise comparison of nearly matching colours. The filters must be so chosen that they convert the response of the instrument into the response curves of the normal eye to the three primaries of the CIE system (thus carrying out the above calculation automatically). Such instruments offer the most promise for rapid and precise comparative measurements. Sensitive photoelectric cells or photomultipliers and high amplification can be used to give a high sensitivity to small differences. Several instruments of this type have received attention in connection with paint matching; e.g. (from the U.S.A.) the Colormaster, the Color-Eye, the Color and Color Difference Meter, and (from the U.K.) the Hilger J40 colorimeter, the Colorcord, and the Colormat.

Even with photoelectric instruments of the highest sensitivity it is difficult to equal the performance of the trained observer in discriminating small colour differences. For the lighter and intermediate colours the sensitivity of the instrument may approach that of the trained eye, but for the darker colours the instrument sensitivity falls because of the decreased amount of light available, whereas the sensitivity of the eye is maintained even in the comparison of deep blacks.

A sensitivity of 0·3 N.B.S. units can be expected in a good spectrophotometer. That of photoelectric colorimeters varies considerably, but does not, at present, exceed 0·3–0·25 N.B.S. units. Such sensitivities, although lower than that of the trained observer, are nevertheless sufficient to indicate colour differences for fairly light and intermediate colours comparable with the tolerances to which it is desired to work in the paint industry*.

An important matter that has to be borne in mind in relating visual and instrumental appraisal is the effect of surface texture. It is possible to "match" a glossy paint by a matt one only to an individual's satisfaction. Exact instrumental work requires close similarity of the level of gloss or mattness as between standard and sample. The extent of the effect is indicated by the fact that passing from a glossy paint surface to a matt one of the "same" colour is equivalent to adding approximately 4% of white light. Thus, dark colours are affected more than light ones, and saturated colours more than less saturated ones.

INSTRUMENTAL AIDS TO MATCHING

How can instruments directly assist the colour matcher? Much work has been carried out at the Paint Research Station on this problem. Some manufacturers have made good progress, but so far the industry predominantly depends on the colour matcher.

As part of the studies so far made, practical matching operations have been followed, paint samples being taken at each stage and the colour matcher's comments and tinter additions noted. Subsequent colorimetric measurements showed how judgment was affected by the three-dimensional nature of colour, expressed, e.g., as hue, lightness, and saturation, no addition of tinting pigment affecting only one of them. For example, it might be thought that a batch correct as to hue and saturation but too dark could be corrected merely by addition of a white pigment paste; in fact that would also decrease the saturation. Conversely, the addition of, e.g., a yellow paste to correct the hue would also increase the lightness. Moreover, the addition of, e.g., a yellow pigment in this way would add more than yellow colour, bringing in some red and green according to the spectral distribution associated with the pigment.

In the following test, measurements were made on small samples taken during the matching process as amounts of individual tinters were

* See discussion— question by Mr. I. Galley.

added in a small-scale trial before attempting to correct the whole batch. The colour was a sea green, an acceptable match having a luminance factor of 31·1%, starting from primary material having a luminance factor of 23·9%. The matcher proceeded by the following steps—

(1) Added a white paste (all additions were made as predispersed pastes), bringing the luminance factor to 29·7%. (Instrumental readings subsequently showed that further addition of white would have been the best next step, but the matcher proceeded differently.)

(2) Added lemon chrome, altering the hue in the wrong direction, but bringing the luminance factor to 30·6%, very near to that required.

(3) Added white, slightly correcting the hue, but reducing the saturation and altering the luminance factor to 33·2%.

(4) Added Prussian blue in two successive amounts. This showed better judgment, helping to correct all three factors at once and reducing the luminance factor to 32·2%.

(5) Added black in two successive amounts, bringing the colour very near to the acceptable match at a luminance factor of 30·7%.

Optical measurements showed that the matcher would have achieved his objective more rapidly if he had gone further with his early additions of white.

In another case, the aim was to produce an olive green of luminance factor 6·1%. The batch started insufficiently blue and too light (8·1%). The matcher proceeded as follows—

(1) Added blue. This was in the right direction for hue, and reduced the luminance factor to 7·3%.

(2) Added red. Here there was confusion between hue and lightness, the idea presumably being to make the colour darker; in fact, it altered the hue slightly in the wrong direction and left the luminance factor at 7·3%.

(3) Added red. The idea behind step 2 persisted and the result was a slight worsening of hue and only a minor change in luminance factor to 7·2%.

(4) Added black. The need to darken the colour was now dominant. The luminance factor decreased to 6·7%, approaching that required, but the hue was affected, becoming too yellow.

(5) and (6) Added successive amounts of blue. This was wholly in the right direction and, with final minor adjustments, corrected the hue and brought the luminance factor to 6·1%.

The general trend of this matching was reasonably sound; it might have been more quickly achieved by an earlier perseverance with additions of blue before other corrections.

These examples illustrate the kind of matching operations it is hoped to shorten. In general, the methods being explored aim at reducing the number of attempts at a match, rather than at the elimination of the colour matcher, whose ability to adjust for technical variations of various kinds is not likely to be easily replaced by mathematics.

One suggestion is to use colorimetric data in an empirical way when dealing with repeated batches of the same paint. This, in its simplest form, requires measurements on a range of mixtures of the ingredients, so that quantities for adjustment of a mill sample to a standard can be deduced. Another method is to go almost the whole way by converting colorimetric differences between sample and standard to quantities of pigments needed to adjust the match—a complicated mathematical procedure—at least to the point of a final minor adjustment by the matcher.

Methods for the conversion of colorimetric data (figures) to quantities of pigments in admixture have been available for some years*. The major difficulty has been the time required to make the complicated calculations—a matter of hours. With the aid of high-speed digital computers, formulae based on absorption and scattering coefficients have recently been developed at the Paint Research Station in a form suitable for programming, and it is possible to compute very quickly the amounts of various pigments required to match a given measured colour, or conversely to compute the colour that would be produced by any mixture of pigments, or to draw up data on the ranges of colour that can be produced by mixing any of these pigments taken in pairs.

By combining precise colour measurement, particularly the use of differential methods for determining small differences between sample and standard, with rapid methods of calculation, it should prove possible to give the colour matcher considerable guidance. Moreover, such calculations are likely to assist in studying the suitability and cost of proposed formulations and may indicate simplification of existing formulae.

* * *

The various investigations described were carried out at the Paint Research Station, and thanks are due to my various colleagues concerned, in particular Miss D. L. Tilleard and Dr. D. R. Duncan. Parts of the first section were originally published in connection with the symposium "Powders in Industry" held by the Society of Chemical Industry in September 1960.

RESEARCH ASSOCIATION OF THE BRITISH PAINT, COLOUR, AND VARNISH ASSOCIATION
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MIDDLESEX

(*MS. received 8th May 1961*)

* In particular, in relation to paint, D. R. Duncan, *J. Oil & Col. Chem. Assocn.*, 32, 296 (1949).

Discussion

Mr. D. T. PRESTON: Which of the colour-measuring systems mentioned in the paper have found the widest acceptance in the paint industry, and to what extent are they employed for day-to-day matching?

Dr. BELL: It is not easy to make a general

statement, except to say that such methods are but little employed in dealing with day-to-day matching. Both spectrophotometry (including abridged spectrophotometry) and tristimulus colorimetry are to be found here and there in the industry, but there is as yet no general development.

Mr. PRESTON: What is the relative ease of colour matching with inorganic pigments as compared with organic pigments?

Dr. BELL: The problems do not lie so much with organic, as against inorganic, pigments, but with freedom from such things as dispersion instability, flotation or bronzing, to which individual pigments, whether organic or inorganic, may be disposed.

Dr. R. MCGREGOR: What additives are used to give thixotropic paints their special properties? Does the physical size and shape of the pigment particles used have any influence on this type of behaviour?

Dr. BELL: Thixotropy in paints can be achieved in various ways, but the full effect, as in some gel paints, is generally associated with specific treatment of the medium. Various degrees of thixotropy and other rheological conditions can be achieved by the selection of particular pigment–extender combinations. Some very fine surface-treated extenders have definite beneficial effects on body and flow of paints, for example. The position is complicated, involving many factors in which both pigment and medium are concerned, and is not so fully understood as to enable the question to be adequately answered directly in terms of size and shape.

Mr. A. MURRAY: Does catalytic fading occur with mixtures of certain pigments in paints? I have noticed that with some green paints the yellow component almost disappears on weathering.

Dr. BELL: There are cases of fading of relatively small amounts of coloured pigment in association with large amounts of whites. Systems deficient in this respect have to be avoided in formulation. In a way the fading could be called catalytic. The particular cases mentioned by Mr. Murray are probably more directly chemical, involving acid attack from polluted atmospheres on particular pigments. However, fairly recent work has shown that the state of oxidation of the medium is important, and that specific agents can have an inhibitive effect.

Dr. W. CARR: Dr. Bell has stressed the importance of the pigment in the physical properties of the wet paint and the paint film, and has described the phenomena of flocculation and flotation, which often occur when mixtures of pigments are used. Both these phenomena usually occur when the pigments in the mixture differ widely in particle size and other physical properties, i.e. when one pigment is organic and the other inorganic. Many surface-active agents have been used on an empirical basis to overcome these troubles but with only limited success.

Recently, however, Professor Overbeek of Holland and his co-workers have attacked the problem from a theoretical basis. Because electrophoresis can take place in non-aqueous systems, such as paints, although the mobilities are much less than in aqueous systems, they have applied to non-aqueous dispersions the principles of aqueous colloidal systems, including electrical double layers, zeta potentials, etc. Their conclusions are both interesting and surprising. For very small particles, the theory leads to the deduction that only powerful anionic surface-active agents, e.g. the well-known dialkyl succinates, will increase dispersion stability; long-chain fatty acids, on the other hand, will reduce the dispersion stability of small particles. For larger particles, the converse is true.

If these conclusions are valid, it would seem that, to prevent flocculation and flotation, one type of surface-active agent is required for the small pigment particles, i.e. organic, and another for the larger, i.e. inorganic. Has Dr. Bell any comments?

DR. BELL: Professor Overbeek's work is extremely interesting, but I should like to learn more of the theories when applied to a wide range of pigment combinations and types in various media, because in practice many factors are involved. I do not think that in practice it is just a matter of small as against large particles, if only because pigments differ so much chemically. Moreover, there is the question of the relationship between different surface-active agents and the media in which they are present. In practical paint systems there can undoubtedly be changes in adsorbed layers with replacement of one active material by another from the medium, on storage or possibly even as the paint film undergoes oxidation. Nevertheless, the indications of Professor Overbeek's work as outlined by Dr. Carr are worthy of considerable study.

Dr. E. ATHERTON: Does Dr. Bell consider that it is possible to use computer methods, as described in the earlier paper by Alderson *et al.*, for colour matching with pigments in paint films.

Dr. BELL: The computer methods described by Alderson *et al.* offer some attractive possibilities in the paint industry. The same basic formulae are applicable, with the difference that there is no substrate to take into account and all measurements are made on films of hiding thickness. Digital computer programmes are available to calculate the relative amounts of four chosen pigments required to match a given colour or, alternatively, the spectrophotometric method can be used for the limited case of tinting a white base paint.

The methods are available, but instrumentation is still expensive and there are a number of technological difficulties. So far only a relatively few industrial concerns have shown interest.

Mr. I. GAILEY: Dr. Bell states that the sensitivity of photoelectric colorimeters does not at present exceed 0·3–0·25 N.B.S. units. This is contrary to claims that have been made for the Colormaster differential colorimeter. When this instrument is used as a comparator to measure small differences between a standard and a sample of the same colour, differences of the order of 0·05 N.B.S. units can be detected, provided that the surfaces of the standard and the sample are smooth and regular. Results obtained with the

Colormaster under these conditions have also been stated to be reproducible to 0·02–0·03 N.B.S. units.

Dr. BELL: The figures given in my paper are in practical terms relative to visual observation, which itself does not provide an absolute standard. In one sense the eye is the only means of checking an instrument, whilst in another sense an instrument is the only means of checking the eye.

The other point is that there is a difference between the sensitivity of the instrument at any given time and the general overall practical sensitivity for colour-matching work with industrial paints applied to specimen panels. My figures really relate to sensitivity in the sense of a sound level of reliability under reasonable practical conditions, with measurements made in relation to a white standard.

It is true that the scale of the Colormaster differential colorimeter can be read (by estimate) to four figures, i.e. to 0·01%, and that a change of less than 0·03% in the scale reading can be detected as a deflection on the null-point meter. Thus it is possible to detect the existence at any one time of very small differences indeed, e.g. variations over the surface of a test panel or between two similar panels.

In measurements relative to a white standard, a number of possible sources of variations may become significant, e.g. very small drifts in the photocell responses, or minor changes in the electrometer measuring circuit, in the lamp emission, or in the temperature of the filters. We have found that the standard deviation of measurements made on a fairly light-coloured uniform panel against a white standard, over a period of two or three weeks, was about $\pm 0{\cdot}15\%$ in X, Y or Z or $\pm 0{\cdot}0003$ in x or y.

The high sensitivity is, of course, of great value in giving something in reserve to cover minor variations in the conditions and in providing for the exploration of non-uniform specimens. We regard, with considerable confidence, the operative figure for our kind of work to be 0·3–0·25 N.B.S. units.

Practical Problems in Preparation and Dyeing of Cross-wound Packages

J. WHITTAKER

Package dyeing is a relatively new but expanding method of advantageously producing dyed yarns for various end-uses. Consideration is given to the principles governing the production and processing of suitable cross-wound packages. Mention is made of some of the problems with which the package dyer is faced and recipes are outlined for overcoming them. Finally the advantages of high-pressure drying are briefly discussed.

Introduction

Despite the increasing interest being shown in package dyeing it is some considerable time since the general principles involved were adequately reviewed. A Symposium on science and craft in coloration seems to provide an opportune occasion, since the process has been established sufficiently recently to take advantage of increasing systematic knowledge and yet is old enough to embody the dyers' traditional skill and craft. It has been said that package dyeing used to be like a New England clambake— you put in the colour and materials, went away for two hours, and hoped for the best. Today, however, in co-operation with technologist, engineer, and chemist, the package dyer has much more confidence in his own art and skill.

In order to confine the scope of this paper cross-wound packages alone are considered, i.e. those specially constructed to facilitate dyeing of the yarn. This will eliminate some of the well-established forms of dyeing package, e.g. cops and beams, but cheeses, cones, muffs, and rockets will provide sufficient claims for attention.

Package dyeing of yarns is usually undertaken to eliminate serious disadvantages of traditional forms of dyeing. Fashion shades can be produced more readily than in the case of raw-stock dyeing, and no spinning difficulties are experienced. The condition of the yarn is more easily preserved than in hank or chain-warp dyeing, thus facilitating subsequent processing. Larger weights per shade can be accommodated than in cop dyeing. Package dyeing also provides an ideal method for the production of coloured woven goods, striped circular knitwear, and jacquard patterns.

FIG. 1

Many problems that are common to other forms of dyeing are found also in package dyeing, but there are others peculiar to it, so that many of the principles involved require fuller explanation. The purpose of this paper is to consider those principles which are peculiar to package dyeing, viz., preparation of the package, the performance of liquor-circulating pumps, the properties of the dyes, and the presentation of the product.

Preparation of the Package

The time and care spent in the preparation of the package play an all-important part in the adequacy of the dyeing. There are two important factors to consider at the outset. A package has to be presented which is equally suited to the requirements of the dyer and to those of the subsequent processor. It is of little use to have a package which reduces the dyer's burden and enables level dyeings to be obtained if it becomes so distorted during processing that the waste is excessive or the subsequent processes become uneconomic.

The mechanical, hydrostatic, and hydraulic forces to which the package is subjected necessitate a special construction, but the shape and size are widely variable (see Fig. 1).

Obviously, a dyehouse which forms part of a vertical organisation can choose the package which most conveniently fits in with the adjacent processes, but a commission dyehouse has to consider a wide variety of customers and chooses that form which can readily be transformed into various others. The ideal package is of uniform density throughout. It should be of sufficiently open construction to permit dye liquor to flow freely, but yet dense enough to prevent channelling of the liquor through more accessible places and consequent failure to dye in others.

The density of any package may be adjusted during the winding process by altering the relation between the rate at which the yarn is laid on the package and the rate at which it moves across the package. The number of layers placed on the package for each time of crossing is known as the "wind". Fig. 2 illustrates one-wind and two-wind packages.

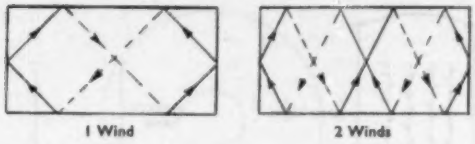

FIG. 2

Basically there are two methods of producing a cross-wound package— surface winding and precision winding. In surface winding the yarn package is formed on a freely rotating spindle which is driven by a spirally grooved roller. Precision winding utilises a positively driven spindle on which the package is mounted. Hairy yarns are more frequently wound on surface-driven packages, and continuous-filament or smooth staple yarns on spindle-driven packages. However, packages of either type of yarn can be successfully wound on both systems.

The factors affecting the density of the package when surface winding are different from those that govern it in precision winding. In surface winding, the number of winds varies as the package diameter increases, but the wind angle (the angle between the direction in which the yarn is laid on the package and the diametrical plane of the package) remains constant. Crossing angles and reversal angles also remain constant, so that if the starting diameter and initial wind are suitably chosen the package structure can be satisfactorily designed. Fig. 3 shows the effect of increasing diameter in surface winding.

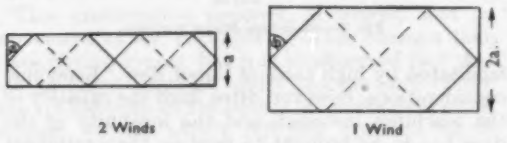

FIG. 3

In precision winding, the number of winds remains constant but the winding angle decreases. The angle of reversal also decreases, so that there is a greater tendency to produce hard-ended packages. In Fig. 4 the effect of increasing diameter on precision-wound packages is illustrated.

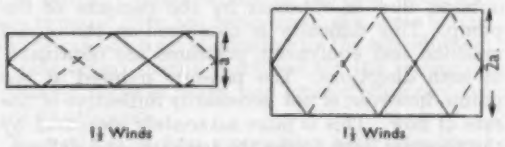

FIG. 4

The yarn supply and its position, speed of winding, winding tension, and the pressure of the package on the winding drum all play an important part in the build of the package, and various devices are available for adjusting their effects in order to increase the possibility of producing packages which are regular and of even density.

If the yarn tension and any fluctuations in it can be reduced to a minimum, softer and more even packages can be prepared at higher speeds. The unwinding accelerator consists of a small metal cone which is inserted into the path of the yarn, reducing ballooning and consequently the yarn tension.

A relief-weight system is available which decreases the pressure of the package on the grooved cylinder as the diameter of the package increases.

It is possible that on, say, each third or fourth successive layer coincident wraps of yarn could be formed. In order to prevent such an occurrence, a yarn-layer displacement device is fitted which continuously displaces the grooved cylinder.

The "soft pressure" attachment for precision-winding machines provides accurate control of tension and distributes pressure evenly over the full length of the package. Despite the efforts of winding-machine designers to minimise the effects of hard ends of a package, it is still possible to find that the density appears to be greater there. A corner-rounding machine minimises this difficulty, which can affect the levelness of dyeing.

In contrast to other package-winders, the rocket winder employs a principle whereby the yarn traverses from the inside to the outside of the package over a distance of approx. 18 in., which mitigates any adverse effect of unevenness of dyeing. Fig. 5 shows diagrammatically the production of a rocket on the Delerue Rocket yarn-package winder.

These general principles and the attachments devised for the production of soft-dyeing cones, cheeses, and mock-cakes have proved an ideal foundation on which to construct specialised machinery designed for the processing of bulked fibres.

Modern reeling machines give cross-wound hanks which produce suitable muffs for dyeing.

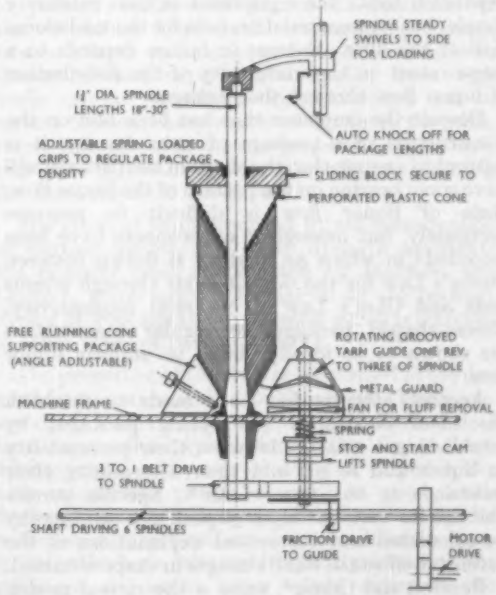
SPINDLE STEADY SWIVELS TO SIDE FOR LOADING
1¼" DIA. SPINDLE LENGTHS 18"-30"
AUTO KNOCK OFF FOR PACKAGE LENGTHS
ADJUSTABLE SPRING LOADED GRIPS TO REGULATE PACKAGE DENSITY
SLIDING BLOCK SECURE TO PERFORATED PLASTIC CONE
FREE RUNNING CONE SUPPORTING PACKAGE (ANGLE ADJUSTABLE)
ROTATING GROOVED YARN GUIDE ONE REV. TO THREE OF SPINDLE
METAL GUARD
MACHINE FRAME
FAN FOR FLUFF REMOVAL
SPRING
STOP AND START CAM LIFTS SPINDLE
3 TO 1 BELT DRIVE TO SPINDLE
SHAFT DRIVING 6 SPINDLES
FRICTION DRIVE TO GUIDE
MOTOR DRIVE

FIG. 5

Over-feeding devices are utilised to ensure that there is little tension as the yarn is taken up. Patent applications have been made for special devices for producing packages in which high-bulk yarns can be adequately dyed with regularity of bulking.

Obviously it will rarely be possible for a single package dyer to produce all types of packages. Nevertheless, it is advisable that he prepares his own packages. Package dyers therefore tend to specialise, and the shape and density of their packages will depend entirely upon the counts or deniers of the different fibres. For cotton, a density of about 300 g/l. is advisable, for wool about 350, and for Courtelle 275. Table I gives the density of a number of packages which have been adequately dyed on cones.

TABLE I

Fibre	Count	Quality	Density (g/l.)
Cotton	1/16s	Combed	305
	1/32s	Combed	304
	1/38s	Combed	290
	1/72s	Combed	275
	2/32s	Combed	324
Cotton/rayon	1/30s	Perro	305
Rayon	1/18s	Ruffray	320
Nylon	1/30s	Spun	360
Cotton/nylon	1/20s	90/10	291
Wool	1/36s	Worsted	343
Courtelle	1/36s	Worsted	265
	2/30s	Worsted	290

Performance of the Liquor-circulating Pumps

The main components of package-dyeing equipment consist of a main dyeing chamber, circulating pump with reversing device, and sometimes an expansion tank; the equipment is thus relatively simple, but its manipulation calls for the traditional skill of the dyer. Success or failure depends to a large extent on the uniformity of the distribution of liquor flow through the packages.

Despite the emphasis that has been laid on the construction of a package of even density, it is natural to assume that the shape of the package will have some bearing on the pattern of the liquor flow. Rate of liquor flow is difficult to measure accurately, but interesting experiments have been recorded[1] in which an analogy is drawn between Darcy's Law for the flow of fluids through porous beds and Ohm's Law of electrical conductivity. Cheese-shaped packages of regular construction are shown to be ideally suited to uniform liquor flow.

Another attempt has been made to establish the ideal conditions for dyeing packages by establishing a relation between their permeability to liquor and to air and then determining their resistance to the flow of air[2]. Specific permeabilities for various shapes of packages can thereby be calculated and theoretical explanations of the extensive effects of small changes in shape obtained.

Boulton and Crank[3], using a theoretical model, have shown that production of level dyeings is facilitated by high rates of liquor flow. Economic considerations, however, often limit the capacity of the machines installed, and the ingenuity of the dyer has to be brought to bear on the equipment which he operates.

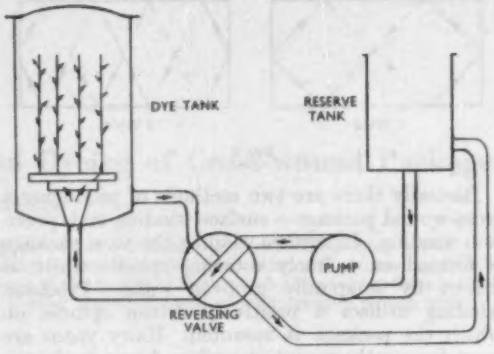

FIG. 6— Totally enclosed dyeing machine

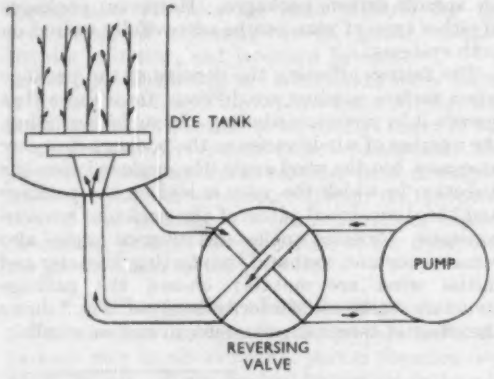

FIG. 7— Open-type dyeing machine

Earlier machines were of two types, closed and open; they are shown diagrammatically in Fig. 6 and 7. The disadvantages of the open machine can readily be seen from Fig. 7; although it is possible to reverse the flow of the liquor, flow is being motivated in one direction only by the suction of the pump. In the reverse direction, i.e. from inside to outside, flow is obtained by the pressure of the pump. This difficulty is overcome in the closed machine and equivalent pressures are obtainable in both directions. The pressure induced at the pump, however, is not necessarily indicative of the rate of flow. This is more accurately measured by the pressure drop across the package, and differentials of 4–5 lb/in^2 have been shown to be adequate.

Much argument arises amongst practical dyers as to the best direction in which to direct the liquor flow. A simple theoretical examination favours pumping from outside to inside. Fig. 8 shows the cross-section and elevation of a dyeing package. Assume that liquor flows at a rate V (in^3/min) from inside to outside. The linear rate of flow past any point A distance r from the centre will be $V/2\pi rl$, where l is the length of the dyeing column. The linear rate of flow is thus inversely proportional to the distance from the centre, and

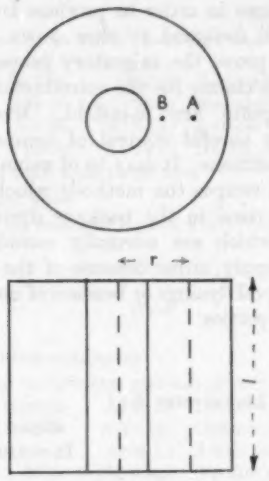

FIG. 8— Top elevation and side elevation of package

the amount of liquor coming into contact with a given point in unit time varies accordingly. If the dye is taken up at the same rate throughout the package, it is clear that the concentration at A will be lower than the concentration at B and uneven dyeing may result because the rate of flow is also decreasing. On the other hand, when the flow is in the reverse direction (outside to inside) these two factors are in opposition and more even dyeing should result.

This examination assumes, of course, that no movement of the packages or other changes take place during dyeing, but it is an observed fact that the packages contract under the pressure of the flow. Variations in the extent of contraction could account for the widely differing opinions which package dyers hold about the advisability of a particular type of flow (in to out; out to in). The difficulties encountered with various fibres are often overcome by alternating the two types of flow, as indicated in the dyeing recipes given later.

The limitations of the centrifugal pump are well known and the reduction in pressure at the temperature of the commercial boil has for a long time proved a disadvantage to the dyer when certain types of dyes are being used. To some extent this defect has been eliminated by the introduction of pressurised dyeing machines for the dyeing of synthetic-polymer fibres, and greater efficiency can now be attained.

Recently axial-flow pumps have been introduced into package dyeing machines, and some operating difficulties have been overcome since they are directly reversible and abolish the need for reversing valves with all the attendant bends and pipings. The efficiency for the same power of motor is thereby increased and an additional contribution to the solution of the level-dyeing problem has been made.

Whatever the shape of package being processed (cones, cheeses, rockets, mock-cakes, and some types of muffs), the packages are loaded on spindles mounted on a carrier which is removable from the main kier. It is essential that there must be flow only directly through the packages and that it is eliminated from all the spaces between packages. Various methods are introduced in order to direct the flow. Some cheeses are loaded so that they make a complete column of yarn on each spindle, but they are then subject to so much pressure that it is not unusual for an excessive reduction in traverse length to result. To prevent this others are wound on springs and have devices that retain the original traverse length. Cones have individual metal separators or intermediates between each package. Muffs of nylon processed by special techniques are often so irregular in shape that they have to be packed "brick" fashion in an annular perforated cage in order to obtain satisfactory levelness of dyeing.

Properties of the Dyes

It should hardly be necessary to reiterate that the dyer's task can have been either made or marred by the technologists who are responsible for preparing the packages or the engineers who control the performance of the pumps; even if these aspects are satisfactory, the dyer's task is only just beginning and has many attendant problems.

The quality of the water used varies greatly with the district in which the dyehouse is located. Whilst many types of dyeing will be affected by the hardness of the water and the impurities in it, the package dyer is faced with high Hazen values and bacteriological content; as his package forms a perfect filter medium, it is not unusual to find deposits of algae or other impurities on the inside or outside of it.

It is usual to give packages a wet treatment before the dyeing process. The solution often contains some of the dyebath auxiliaries in order to present surfaces of equivalent condition to the circulating dyes. Such wetting-out processes, however, have to be adjusted for different fibres; theoretical and experimental studies have been made of the swelling action, resistance due to surface tension, compression of the air in the yarn, yarn count, rate of flow, static pressure, temperature, and types of wetting agents in an effort to establish the most suitable conditions [4].

The effect of foam produced by the introduction of wetting agents and other dyebath assistants has recently been investigated by Hadfield and Lemin [5]; much useful information on the package dyeing of wool has been presented which is relevant to other types of package dyeing.

The properties of the dyes are described in the dye manufacturers' technical publications. The package dyer, however, has a much more limited field than most other dyers. Suitability for package dyeing implies adequate solubility or dispersibility and exceptional purity, as well as good level-dyeing properties. Deposits of undissolved dye or undispersed pigment or impure diluents (e.g. impure Glauber's salt) are frequently found on the packages and spoil what would otherwise be perfectly level dyeings.

A wide choice of different brands of the same dye is often available, e.g. of vat dyes. None of them contains any magic formula for level dyeing, and choice is often made (except in the case of dispersion processes) on the basis of the physical properties of non-dusting, ease of storage, and so on, rather than the particle size. (It has been shown that at vat-dyeing temperatures the dye in the leuco form appears to be unimolecular and fully dissociated [6].)

Representative Dyeing Procedures

It would be impossible to discuss fully all the refinements which the package dyer introduces into his recipes in order to produce level dyeings. They are all designed to slow down the rate of strike or improve the migratory properties of the dye, and the claims for the introduction of special levelling agents are manifold. Much can be achieved by careful control of temperature and dyebath conditions. It may be of value to illustrate from actual recipes the methods which have been successfully used in the package dyeing of yarns with dyes which are normally considered to be difficult to apply, either because of the difficulty of producing level dyeings or because of unsatisfactory fastness properties.

Vat Dyes on Cotton

Vat Green — Cotton: 400 lb (181·6 kg) — Liquor ratio 10 : 1

			Liquor flow
(*a*) Bleach with peroxide			In to Out 1 h
35 pints	(19·88 l.)	H_2O_2 35%	
6 pints	(3·40 l.)	Sodium silicate J81 (41·6° Bé)	
6 pints	(3·40 l.)	NaOH 100°Tw (48° Bé)	
(*b*) Cold wash and warm wash			In to Out 5 min
(*c*) Dye by leuco method at 112°F			Out to In 1 h
3 oz 12 drm	(106 g)	Caledon Jade Green XN 1000% (ICI)	
14 drm	(24·8 g)	Paradone Yellow GC 360% (LBH)	
25 pints	(14·20 l.)	NaOH 100° Tw	
20 lb	(9·07 kg)	Sodium hydrosulphite	
10 lb	(4·54 kg)	Glue powder	
(*d*) Vacuum extract until fully oxidised			
(*e*) Cold wash and warm wash			In to Out 5 min
(*f*) Soap boil			In to Out 15 min

Azoic Dyes on Cotton

Azoic Red — Cotton: 100 lb (45·4 kg) — Liquor ratio 10 : 1

			Liquor flow
(*a*) Boil out with Teepol (sulphonated fatty alcohol)			In to Out 10 min
(*b*) Cold wash			In to Out 2 min
(*c*) Impregnate			Out to In 10 min In to Out 10 min Out to In 10 min
2 lb 6 oz	(1·08 kg)	Brenthol BN (ICI)	
3 pints	(1·70 l.)	Azomel A (ICI)	
10 pints	(5·68 l.)	NaOH 100° Tw	
20 lb	(9·07 kg)	Sodium chloride	
(*d*) Vacuum extract lightly (1 min)			
(*e*) Sodium chloride (20 lb) (9·07 kg) wash			1 min each way for 2 min
(*f*) Vacuum extract (1 min)			
(*g*) Developing			5 min each way for 30 min
2 lb 8 oz	(1·13 kg)	Brentamine Fast Scarlet G Base (ICI)	
4 pints	(2·27 l.)	Azopol A (ICI)	
4 pints	(2·27 l.)	HCl conc.	
1 lb 4 oz	(567 g)	Sodium nitrite	
1½ pints	(852 m)	Acetic acid 80%	
(*h*) Cold wash			In to Out 2 min
(*i*) Boil with soap			In to Out 15 min
(*j*) Boil with Albaclin WL (DH) (detergent)			In to Out 10 min

Reactive Dyes on Cotton

Pale Blue — Cotton: 350 lb (158·9 kg) — Liquor ratio 10 : 1

	Liquor flow
(*a*) Bleach	In to Out 1 h
(*b*) Cold wash	In to Out 2 min
(*c*) Warm wash	In to Out 2 min

REACTIVE DYES ON COTTON—*continued*

(*d*)	Dye cold to 140°F (in 30 min) and maintain there		Out to In (6 min) In to Out (4 min) }	for 1½ h
	1 lb 1 oz	(482 g)	Remazol Brilliant Blue R (FH)	
	10½ oz	(298 g)	Remazol Turquoise Blue G (FH)	
	200 lb	(90·7 kg)	Sodium chloride	
	2 pints	(1·14 l.)	NaOH 100° Tw	
(*e*)	Cold wash with acetic acid			In to Out 5 min
(*f*)	Warm wash			
(*g*)	Boiling soap and Irgavel S (Gy) (lubricant)			In to Out 15 min

ACID DYES ON WOOL

Wine Wool: 350 lb (158·9 kg) Liquor ratio 10 : 1

				Liquor flow
(*a*)	Circulate auxiliaries			1 min each way for 10 min
(*b*)	Raise temperature and introduce dye at 120°F			
	6 pints	(3·40 l.)	Univadine W (Ciba)	
	15 lb	(6·80 kg)	Cyanine Fast Red 3GP (LBH)	
	6 pints	(3·40 l.)	Acetic acid 80%	
	30 lb	(13·6 kg)	Glauber's salt (anhyd.)	
(*c*)	Raise to boil (2 deg F rise/min)			In to Out 40 min
(*d*)	Boil			In to Out 45 min
(*e*)	Extract			
(*f*)	Warm wash at 140°F with Irgavel S (Gy)			In to Out 5 min

REACTIVE DYES ON NYLON (MUFFS)

Leaf green Nylon: 60 lb (27·24 kg) Liquor ratio 17 : 1

				Liquor flow
(*a*)	Boil out with Lissapol N (ICI)			In to Out 10 min
(*b*)	Dye with—			
	2 lb	(907 g)	Procion Brilliant Yellow 6G (ICI)	
	¾ lb	(340 g)	Procion Brilliant Blue R (ICI)	
	3 pints	(1·70 l.)	Formic acid (85%)	
	½ lb	(227 g)	Irgasol DA (Gy)	
(*c*)	Start cold			Out to In 5 min
(*d*)	Raise to boil			In to Out 30 min
(*e*)	Boil		Out to In (5 min) In to Out (5 min) }	for 30 min
(*f*)	Soap and soften with Irgamin TP (Gy)			

PHTHALOGEN DYES ON COTTON

Peacock blue Cotton: 80 lb (36·29 kg) Liquor ratio 12 : 1

				Liquor flow
(*a*)	Bleach (as for vat dyes) with addition of—			
	1 lb 6 oz	(624 g)	Phthalofix FN (FBy)	In to Out 1 h
	10 lb	(4·54 kg)	Glauber's salt (anhyd.)	
(*b*)	Wash twice with Glauber's salt (10 lb)			
(*c*)	Paste with—			
	3 lb	(1·36 kg)	Phthalogen Blue IF3GK (FBy)	
	5 lb	(2·27 kg)	Levasol DG (dispersing agent) (FBy)	
	15 lb	(6·81 kg)	Acetic acid (glacial)	Stand for 20 min
(*d*)	Set dyebath cold with—			
	14 oz	(397 g)	Emulsifier W (FBy)	
	1½ lb	(680 g)	Aquamollin BCS (dispersing and levelling agent) (CFM)	
	1¾ lb	(794 g)	Acetic acid 80%	Out to In (6 min) In to Out (4 min) } for 1 h
(*e*)	Vacuum extract			
(*f*)	Cold wash twice			In to Out 5 min
(*g*)	Develop with—			
	3 lb	(1·36 kg)	NaOH 100° Tw	
	2 lb	(907 g)	Sodium hydrosulphite	
	1 lb	(454 g)	Naphthopan E (developer) (FBy)	
(*h*)	Wash twice			In to Out 5 min
(*i*)	Soap			In to Out 5 min

MODIFIED BASIC DYES ON COURTELLE

Dark grey Courtelle: 60 lb (27·24 kg) Liquor ratio 17 : 1

				Liquor flow
(*a*)	Pretreat with—			
			1/1000 Emulsifier OC (Ciba)	
			1/1000 Sodium acetate	
(*b*)	Raise from cold to 170°F over 20 min			In to Out 20 min
(*c*)	Add 1/1000 acetic acid 80%			
(*d*)	Dye with—			
	13½ oz	(383 g)	Deorlene Blue E5G (CAC)	
	12 oz	(340 g)	Astrazon Blue 3RL (FBy)	
	2 lb 10 oz	(1·19 kg)	Sevron Red L (DuP)	
	2 lb 4 oz	(1·02 kg)	Sevron Yellow 3RL (DuP)	Out to In 10 min
(*e*)	Raise to boil (over 90 min, boil for 30 min)			Out to In (6 min) } for 2 h In to Out (4 min) }
(*f*)	Cool to 140°F (over 20 min)			
(*g*)	Finish at 140°F with—			
	6 pints	(3·40 l.)	Azopol A (ICI)	
	2 lb	(907 g)	Alcamine extra (Allied Colloids)	In to Out 15 min

Presentation of the Package

Having done his utmost to ensure that the package is adequately dyed, the dyer has still to see that the other essential property, its stability, is preserved. Upon his handling depends to a large extent the efficiency of the subsequent processes. At one time there was no alternative but to unload individual packages from the dyeing spindles and, after removing a large proportion of the moisture by hydroextraction, stack them in cabinet dryers so that hot air could be circulated around them. When it is realised that the packages were handled several times and were in contact with unfiltered air for long periods (20 h for cotton) it can be seen that the results were surprisingly good. Fig. 9 shows the rate of removal of moisture from packages in a typical cabinet dryer.

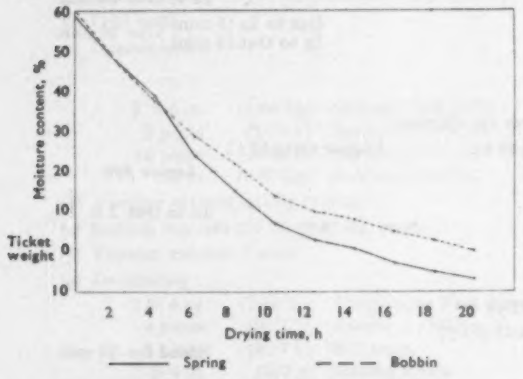

FIG. 9— Rate of removal of moisture in dyehouse stove at average temp. of 200°F

Progress in this field has been very rapid, improvements in drying efficiency having been made in the port dryer (8 h), the pressure-extractor dryer (3 h), the semi-rapid dryer (2 h) to the rapid dryer (1 h), and some explanation of the principles of drying is necessary.

Any drying process is based upon the principle of heat exchange; shorter drying times are obtained by the introduction of more heat energy. The heat energy is, however, proportional to the weight of air. Four times the amount of heat energy can be fed to the packages by the same volume of air at 32 lb/in² as at atmospheric pressure. At 85 lb/in² eight times as much heat energy is available as at atmospheric pressure without the need to increase the size of the blower.

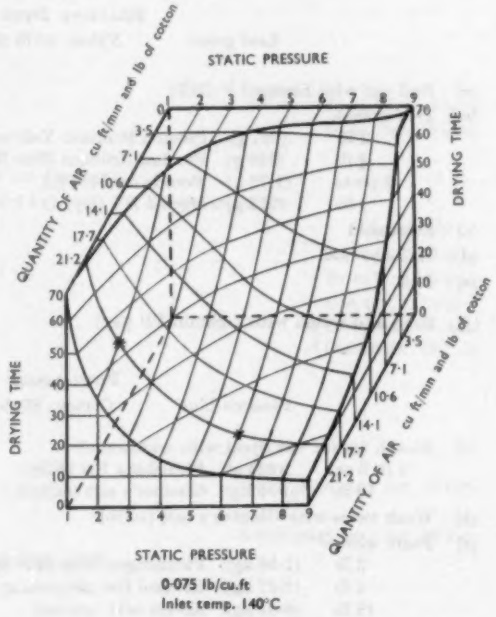

FIG. 10

Recker[7] has established the effect of static pressure on drying times. Fig. 10 relates drying time to static pressure and quantity of air delivered. In this three-dimensional graph, drying time is measured vertically, static pressure horizontally, and amount of air per pound of cotton on the horizontal lines which give depth to the cube. The drying times are not reduced in the same proportion as the heat absorption capacity of the air is increased. At 2 atmos. and 21·2 ft³/min, 2·2 lb of yarn are dried in 43 min, whereas at

6 atmos. and 21·2 ft³/min the same quantity is dried in 15 min.

Fig. 11 is a schematic diagram of a typical dryer. The yarn carrier is lowered into the drying chamber; the quick-acting lid closes in a very short time. The compressed air is turned on and the pneumatic gasket seals the lid. The compressed air valve is opened and within a few minutes the static pressure in the system rises to a maximum

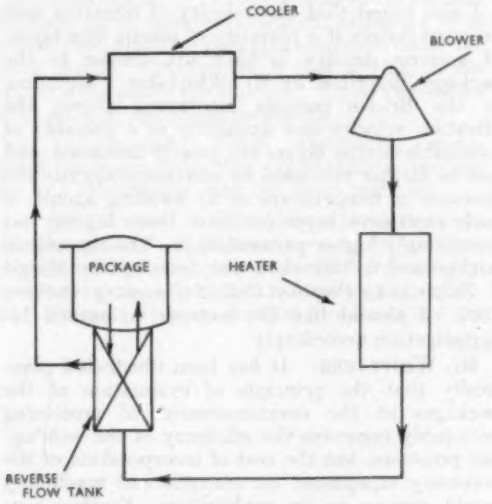

FIG. 11— Principle of static-pressure rapid dryer

which is maintained throughout the drying operation. The blower is started and a rapid flow of air circulates through the packages from outside to inside. Much of the water in the yarn is "squeezed" out mechanically and entrained in the air which carries it to the condenser–water separator.

Extraction takes 15–20 min and is mostly undertaken at full drying temperatures so that there is a gradual transition from mechanical extraction to pure evaporation. The moisture from the yarn is carried away as steam to the condenser, where it is separated.

The drying process is dependent to a large extent not only on the static pressure and air inlet temperature, but also on the air temperature at the outlet from the condenser and the flow reversal procedure used. Different fibres, different packages, and different dyes and finishes all have their individual effects upon the drying times.

Frequently the dyed package requires no more attention than the replacement of the dyeing former by a suitable one on which to despatch the goods to the customer. In other cases rewinding on to tapered cones is necessary, and this gives the dyer an opportunity to assess whether the dyeing is completely satisfactory. In control methods, six test pads made from various parts of each dyed package or knitted swatches from cones from different positions in a batch are examined.

Package dyeing has progressed to such an extent that not only is it used for coloured woven goods and jacquard knitting patterns, but also for solid double-jersey fabrics; perhaps only in the dyeing of yarn for gaberdine cloths or solid weft-faced fabrics does the technique still require perfecting. More experience and some experiment will ensure that package dyeing maintains its popularity in the future, yielding level dyeings of fast dyes on larger packages with adequate fastness.

* * *

My thanks are due to all my colleagues who have contributed to the contents of this paper.

ROBINSON BROS. LTD
SALISBURY DYEWORKS
BLACKBURN
LANCS

(*MS. received 12th June 1961*)

References

[1] Denton, *J. Textile Inst.*, **50**, T521 (1959).
[2] Moss (Shirley Institute), private communication.
[3] Boulton and Crank, J.S.D.C., **68**, 109 (1952).
[4] Denton (Shirley Institute), private communication.
[5] Hadfield and Lemin, J.S.D.C., **77**, 198 (1961).
[6] Marshall and Peters, *ibid.*, **68**, 289 (1952).
[7] Recker, private communication.

Discussion

Mr. D. MARIAN: Has Mr. Whittaker found in his experience that the use of two-way flow offers advantages over methods employing flow only from inside to outside?

Mr. WHITTAKER: Two-way flow offers advantages over one-way flow in respect of all the limitations arising from hard packages, low rates of flow, and dyes with poor levelling properties.

Dr. A. F. KERTESS: Mr. Whittaker referred to the rubbing fastness of the dyed materials. He mentioned that the cheeses are air-dried immediately after dyeing. Has it not been found essential to wash them with soap or other detergents to improve the rubbing fastness?

Mr. WHITTAKER: A close study of the dyeing recipes outlined in the paper indicates that soaping aftertreatments are an integral part of the processing in package dyeing with fast dyes. After repeated treatments a stage is reached when little additional improvement in rubbing fastness is attained and further treatment becomes uneconomic.

Dr. G. H. CRAWSHAW: Mr. Whittaker mentioned the desirability of using large packages, and presumably he would favour the rocket on grounds of size. A casual inspection suggests, however, that the tapered ends of the rocket package are not conducive to uniform liquor circulation and that its use might be restricted to dyes with good levelling properties. Could Mr. Whittaker enlarge on his experience with such packages?

Mr. WHITTAKER: The size of the rocket packages certainly shows advantages of processing and handling but, as the questioner concludes, non-uniform liquor circulation is likely to arise at the tapered ends and special techniques are employed to minimise it. Economic considerations as well as difficulties of 'mending' inside–outside variation

may prevent any rapid replacement of standard packages by rockets.

Dr. J. K. SKELLY: Brief reference has been made in the paper to the formers used for dyeing cross-wound packages. Have polypropylene or high-pressure polyethylene formers been considered for this purpose?

Mr. WHITTAKER: Perforated polypropylene cones are in use as formers on which the packages can be wound directly. Claims made for their durability and efficiency have not been fully verified under continuous processing conditions. Special intermediates have also to be used, and where stainless steel formers are already in use the plastic formers offer little advantage.

Dr. SKELLY: When rapid dryers are used to dry packages, is there not a danger of over-drying in such closed systems? What steps can be taken to prevent this when a large load of cross-wound packages is being dried?

Mr. WHITTAKER: The dangers of overdrying in rapid high-pressure systems are no greater than in conventional dryers. The temperature of the air fed to the packages is controlled, as also is the outlet temperature of the cooling water, so that a minimum quantity of moisture can be maintained in the system; it is then impossible to over-dry the yarns.

Mr. H. R. HADFIELD: In the paper Mr. Whittaker gives various examples of liquor flow. Sometimes it is from out to in, sometimes from in to out. It would be interesting to arrive at a general principle. It is my belief that the deciding principle is the behaviour of the package during dyeing. With in-to-out flow, the dye liquor tends to expand the package and therefore to maintain the seal. With out-to-in flow, the dye liquor tends to compress the package and therefore to favour channelling. If the package is very stable and there is little shrinkage, then the obvious advantages of out-to-in flow can be utilised, although it is my view that these advantages are much less than are generally thought. If, however, the package is not stable, in-to-out flow is to be preferred, as it is much more likely to maintain the seal than to gain whatever slight advantage may result from an out-to-in flow.

Mr. WHITTAKER: Mr. Hadfield rightly concludes that the most suitable direction of flow is dependent on the stability of the package during the dyeing processes. This stability varies with the nature, count, and properties of the fibre and no general rule can be established. An ideal package of yarn could best be dyed from outside to inside.

Dr. L. ZAKARIAS: I am fully in agreement with Mr. Whittaker that the dyeing of cross-wound packages is, like dyeing in general, essentially a filtration problem. Accordingly the practical results could be generally and radically improved by consideration of my work on "Kolloidfiltration (Druckdialyse und Quellungsfiltration)" published in *Kolloid-Zeitschrift*, **37**, No. 1, 50–58 (1925) and of the new collective chemical permeability laws and processes embodied in our patents *BP* 776,967; *BP* 825,002; and partly in *BP* 811,570 (centrifugal and compression dyeing machines, etc.).

In my paper published in 1925 I disclosed that, after the filter media had been moderately evacuated and then saturated in this vacuum with freshly boiled water, a permanent improved filtration effect was achieved, even after the vacuum had been released, whereas previously the filtration velocity was low and very irregular. The velocity was increased ten-fold. This evacuation method is now protected for dyeing and washing fabrics.

I also found that the velocity of filtration falls proportionately if a plurality of plastic film layers of uniform density is built up, similar to the packages described by Mr. Whittaker. According to the British patents mentioned above, the filtration velocity and dyeability of a plurality of extensible textile layers are greatly increased, and can be further increased by increasing slightly the pressure or temperature or by swelling agents, if each successive layer (at least three layers) has increasingly higher permeability. The theoretical background to this work was described by Margit J. Zakarias in *Practical Colloid Chemistry*, October 1959. I should like the lecturer to extend his investigation accordingly.

Mr. WHITTAKER: It has been illustrated practically that the principle of evacuation of the packages at the commencement of processing noticeably improves the efficiency of the wetting-out processes, but the cost of incorporation of the necessary equipment on conventional machinery would appear to be prohibitive. Further consideration of the permeability laws might enable beneficial results to be obtained in package dyeing.

Mr. J. BOULTON: Mr. Whittaker has made reference to the theoretical package-dyeing model of Boulton and Crank and has drawn attention to one of the predictions of this model that level dyeings are encouraged by high rates of liquor flow. Armfield, Boulton, and Crank (J.S.D.C., **72**, 278 (1956)) showed that the predictions from this model were correct and a very important one was that the lowest practicable volume ratio was advantageous and that, e.g., a 6-volume dyeing was always more level than a 20-volume dyeing.

Mr. WHITTAKER: Confirmation of the effect of liquor ratio arises from the package dyers' oft-repeated requests for the preparation of a lot of small packages rather than a few large packages when dyeing small sets in long liquor. It is more difficult to dye standard packages at 20 : 1 than at 7·5 : 1.

Mr. P. S. BEECHING*: The behaviour of the cake in acting as a filter to the dye seems to be a major problem only if the yarn is actually dyed to differing intensities. Can yarn sizing reduce the rate of uptake and so assist in levelling?

Can surface-active materials assist in helping the dye particles not actively dyeing the first area of yarn approached to slide over the yarn surface and so avoid being trapped by the yarn filter? Materials having these effects might assist smoother dyeing throughout the cake.

Mr. WHITTAKER*: Various auxiliaries are utilised to disperse further the dye particles which might

be filtered out by the package. Animal glue has long been utilised for retarding the uptake of vat dyes to assist levelling. There does not seem to be any evidence that the mechanism includes the sliding of the dye particles over the yarn.

Mr. T. FLANAGAN*: Does the very rapid drying rate cause shrinkage differences within the package, which, in turn, could cause tension differences in the cloth?

Mr. WHITTAKER*: No adverse effects of uneven shrinkage have been experienced, although it is possible that unstable packages would be distorted during drying, with the result that setting of the fibres in some places could occur. These variations would show in the fabric produced.

Mr. FLANAGAN*: When vat-dyeing cross-wound packages, does the pigmentation process offer any advantages over the leuco method?

Mr. WHITTAKER*: Our observations indicate that the process of pigmentation gives unlevel deposition of dye, the extent of which is distinctly decreased by the subsequent reduction and oxidation. There is little doubt that dye deposited on a particular part of the package during pigmentation is finally fixed on a different part. It would appear that problems of obtaining a level pigmentation of the package are as great as those appertaining to the leuco dye.

Mr. FLANAGAN*: Has Mr. Whittaker had any success with dyeing the cold-dyeing reactive dyes by the hot bicarbonate method?

Mr. WHITTAKER*: In view of the very poor results which this method yields on cotton yarns we have not used it for the cold-dyeing reactive dyes.

Mr. R. L. JONES*: Has Mr. Whittaker any experience of the sponge-core method of dyeing as applied to synthetic-fibre yarns, and if so what hardness (°Shore) would he recommend for the wound packages?

Mr. WHITTAKER*: Earlier attempts to dye bulked yarns on soft formers which allowed for shrinkage have been superseded by the special winding techniques to give packages which, when processed, preserve the characteristics required. No recommendation can therefore be given for sponge-core techniques.

* Communicated

FRIDAY MORNING, 22nd SEPTEMBER 1961

Chairman— Mr. R. K. FOURNESS

Application of Vat Colorants to Courtelle and its Blends with Cellulosic Fibres

R. J. HANNAY and others

The development is described of a method for the application of vat dyes by a resist technique to fabrics containing acrylic fibres. Satisfactory resist prints were obtained on 100% Courtelle and on Courtelle–cellulosic fibre fabrics in which the Courtelle content was 50–66%. Under the conditions used, a two-stage padding process was found to be preferable to a single-stage one in the production of the vat-dye ground. Although satisfactory white resists could be obtained, it was not possible to produce coloured ones on blend fabrics. Preliminary work on the extension of the method to dyeing is described.

The coloration of fabrics made from synthetic-polymer fibres so as to yield maximum all-round fastness has presented a number of problems to the textile dyer and printer. These problems have been overcome to a certain extent by the development of new techniques and new dyes specially prepared for application to these fibres, but there still remain practical problems connected with individual types of fibre which are by no means completely solved.

The work described here originated as a result of enquiries about a practical method of producing discharge prints on fabrics of acrylic fibres and of blends of acrylic fibres with cellulosic fibres. The range of dischargeable dyes available for the dyeing of acrylic fibres is strictly limited and, even when suitable dyes are found, the hydrophobic nature of the fibre raises practical difficulties in ensuring complete discharge of the dye. In addition, many of the decomposition products produced in discharging the dye still have an affinity for the fibre, which makes their removal very difficult. It is, therefore, almost impossible to be sure that repeatable results showing a good white discharge will be achieved.

Two methods are available for the production of similar effects— blotch printing and resist printing. The former method can yield satisfactory results with certain types of patterns, but with others the results are not so good, and for fabrics containing cellulosic fibres, in addition to acrylic fibres, it is very difficult to achieve, by the direct print-on technique, results which will show high all-round fastness.

These considerations led us to believe that the desired results would best be achieved by a resist technique. The fastness properties of vat dyes on acrylic fibres are exceptionally good, and in direct printing satisfactory results can be obtained by the normal alkaline sulphoxylate technique; on cellulosic fibres, good resists can be obtained under vat dyes by using Leucotrope O (Br). It was therefore considered that such a system was well worth investigating in connection with the coloration of fabrics containing acrylic fibres.

Commercial Leucotrope O is not a particularly pure product and has a rather objectionable smell which makes its use in the colour shop and print room unpleasant. The first problem, therefore, was to find a resist agent which would be satisfactory for use in the works with vat dyes and which would overcome the objections to the application of Leucotrope O. A series of experiments was conducted with a variety of quaternary ammonium compounds, and several of these were found to be capable of producing excellent resists; in addition, they were odourless and convenient to handle. We finally selected one of these compounds as being the most suitable and carried out laboratory experiments into the printing of this resist followed by the padding of the printed fabric with vat dyes and subsequent fixation by means of a steaming process, the method used being an adaptation of the pad–steam process of vat dyeing.

This work threw into relief several practical problems, some of which were already familiar and others new. The familiar problems were those relating to the production of solid level dyeings by the pad–steam process, whilst the new problems were concerned mainly with the preparation of a suitable print paste for the application of the resist. Our attention was first focused on the latter problems, which were connected with the incompatibility of a cationic resist with the normal thickening agents used in printing, which are largely anionic in character. Thus it was found that starch, natural gums, and even a number of the newer modified starches gave printing pastes which separated on standing, or in which the thickening material or the resist agent, or both, was quickly thrown out of suspension or solution. In some cases, even when no obvious separation or precipitation took place, the physical characteristics of the printing paste were altered in such a way as to give poor furnishing properties, resulting in poor resists.

So far we have been unable to find a thickening agent which is cationic in character, but an examination of several non-ionic thickening agents indicates that a suitable choice in this range would produce a printing paste which is stable and has satisfactory printing properties when the resist agent is incorporated in it. The thickening agent which we used in our own experimental work and which gave satisfactory results was Natrosol 250 Low (Hercules Powder Co.), a non-ionic etherified starch. The print paste exhibited a certain tendency to foam in the colour box owing to the mechanical action of the furnishing roller, and this could result in unsatisfactory prints. However, the difficulty

was overcome by the introduction of a small proportion of a silicone anti-foaming agent.

Experiments carried out on a works-scale roller-printing machine, as well as with screens, indicated that very satisfactory resist prints could be obtained by the above technique on fabrics composed of 100% Courtelle, and on blends of Courtelle and cellulosic fibres in which the Courtelle content varied between 50 and 66%.

Our attention was then turned to the production of the vat-dye ground on the printed fabric. It was decided that, in order to maintain sharpness of definition of the print and maximum resist effect, it would be preferable to adopt a single-stage padding process with a liquor containing vat dye and alkaline reducing agent, rather than a two-stage process of pigment padding followed by padding through a fixing solution. Experiments on the single-stage process showed that excellent resist effects could be obtained, but there was always a danger of producing mealy or uneven results owing to the instability of the vat dye dispersion in presence of large quantities of electrolytes. This is a problem which has been presenting difficulties for some considerable time in ordinary dyeing techniques, and to the best of our knowledge has not yet been fully overcome, but there is no doubt that if it could be overcome, the single-stage padding procedure would give the greatest sharpness of definition of the print. On the other hand, a single-stage process produces considerably more wastage of chemicals (reducing agent and alkali) in cleaning out and washing down when changing colours, since in a two-stage padding process the same fixing bath can be used for a continuous run, including a variety of ground colours. The two-stage process also has the advantage that, when steaming takes place without intermediate drying, continuous running can be achieved in the steamer, thus saving time, labour, and steam.

Since good results in colour yield and fixation are obtainable by the pad–steam process, the possibility was not overlooked of using this technique as a straight dyeing procedure for acrylic fabrics, and this aspect will be dealt with later.

The next stage consisted of a series of experiments on the two-stage padding process, in which the printed cloth was padded with a dispersion of vat dye, dried, padded with a solution of alkaline reducing agent, and then steamed for 12 min in a festoon steamer without intermediate drying. A more level and better ground was achieved than with the single-stage process under the particular conditions used, and a number of lengths of cloth, both of 100% Courtelle and of Courtelle–Fibro blend (67/33), were processed by this technique. The actual method was as follows.

The grey-state cloth was first de-sized in a winch with a 1·5% malt solution for 30 min at 60°C and then scoured for 30 min at 40°C in a solution of 0·5% Lissapol N (ICI) to which had been added 500 p.p.m. of 80% acetic acid to ensure that the cloth was not dried under alkaline conditions. After being scoured, the cloth was rinsed well in clean water; it was then festoon-dried and steamed-off on a clip stenter. A stock solution of printing thickening was prepared by sprinkling 10 lb of Natrosol 250 Low into 5 gal of cold water whilst stirring, and leaving the mixture to stand overnight. The print paste had the following composition—

	Weight (lb)	Composition (%)
Natrosol 250 Low (Hercules Powder Co.) (20% stock solution)	37·5	50
Arquad 16/50 (Armour Hess)	30·0	40
Silcolapse 437 (ICI)	(14 ml— i.e., 400 p.p.m.)	
Water	7·5	10
	75·0	100

The silicone anti-foaming agent was carefully diluted with 227 ml (0·5 lb) of water, and this emulsion was stirred into the thickening. The remainder of the water was added, and finally the resist. The prepared print resist was printed on a roller-printing machine with a crush roller following the printing roller, using a printing paste in the colour box of the crush roller made by diluting the above Natrosol 20% stock solution with an equal volume of water. The use of a crush roller gave excellent penetration and helped to minimise any risk of marking-off during the padding treatment. After being printed and dried, the material was then pigment-padded with a paste of dispersed vat dye containing 1% of Indalca UBV (Cesalpina). This was prepared by stirring 5 lb of Indalca UBV into 10 gal of water at 40°C, the mixture being stirred for a further 2 h and then strained. 20% of this solution was added to the padding bath.

Pigment-padding baths were made up to a total weight of 50 lb as follows—

	Weight of substance (lb)				
Caledon Yellow 5G (Paste) (C.I. Vat Yellow 2)	3				
Cibanone Golden Yellow FGK (Paste) (Ciba)		1·5			
Ciba Blue 2B (Paste) (C.I. Vat Blue 5)			3		
Durindone Printing Scarlet YS (Paste) (C.I. Vat Red 45)				3	
Ciba Printing Black FTL (Paste) (Ciba)					1
Water	34·5	36	34·5	34·5	36·5
Indalca UBV (5%) (Cesalpina)	10	10	10	10	10
Sodium carbonate (anhyd.)	2·5	2·5	2·5	2·5	2·5

The padding liquors were prepared as follows. The sodium carbonate was dissolved in 20 lb of water. The remaining water was used to dilute the pigment paste, this mixture was stirred into the thickener, and the solution of carbonate was filtered in. The printed cloth was padded (1 nip)

through a mangle with neoprene bowls (top and bottom) to give as high a pick-up as possible. The actual pick-up was not determined, but was probably in the region of 60–80% on the 100% Courtelle and 80–100% on the Courtelle–Fibro blend. The padded cloth was passed through a pin stenter running in series with the mangle, and dried at a temperature of 135°C (275°F). After being dried, the cloth was again padded through a single-nip padding machine, the bottom bowl of which was metal and the top bowl hardened rubber, the cloth being padded face down. The padding liquor had the following composition—

Formosul (Br)	12·5 lb
sodium carbonate	10·0 lb
sodium sulphate (cryst.)	8·0 lb
water	to bulk of 10 gal

The padding mangle was immediately in front of a festoon steamer, into which the padded cloth was continuously fed, the duration of steaming being 12 min at 100–102°C. After being steamed, the cloth was oxidised in a winch in a solution containing

hydrogen peroxide (20 vol.)	0·5%
acetic acid (80%)	0·15%

the treatment being continued for 15 min at 98°C, after which the bath was slowly cooled to below 70°C. The cloth was then washed in a bath containing 0·2% Lissapol N for 30 min at 98°C; the bath was allowed to cool from 98 to 70°C, and was then cooled to 40°C by flooding-off, the cloth finally being rinsed in clean water. The 100% Courtelle was given a softening treatment in the winch with 2% (on wt. of cloth) of Alcamine Extra (Allied Colloids) at a liquor ratio of 40:1 for 20 min at 45°C. The cloth was hydro-extracted without being rinsed, and then dried.

Although white resists can be produced by the above method, no suitable dyes have yet been found which will enable coloured resists to be produced on fabrics made from blends of Courtelle and cellulosic fibres. A limited number of basic dyes which are resistant to reducing agents and which have affinity for Courtelle gave promising results on 100% Courtelle fabric. Multicolour effects can be produced on both types of fabric by printing ordinary vat dyes in full depths on top of the ground, in conjunction with the white resist print.

The speed of dyeing and the ground colours obtained suggested, as previously mentioned, that this might be a useful method for dyeing these types of fabric; dyeing experiments have been carried out using the two-stage process. The advantages of this technique over present methods are the very high, all-round fastness of the finished dyeing, the retention of the excellent handling and draping properties of the finished fabrics, and the short processing time, which should offer considerable saving in production costs in comparison with the much longer times of dyeing that are usually required for the production of dyeings employing basic and disperse dyes on 100% Courtelle, or these dyes in conjunction with dyes for cellulose on blended fabrics. In addition, vat dyes will cover both cellulosic and acrylic fibres in blended-fibre fabric, whereas at present two entirely different types of dye are required to produce solid dyeings on such mixtures.

A preliminary examination of the range of vat dyes does indicate, however, that certain dyes will colour the acrylic fibre more deeply than the cellulosic one, some act in the opposite manner, and others give a fairly solid dyeing. The classification of dyes for this purpose is a long and laborious task and is one which is really in the field of the dye manufacturer, but the general indications from the limited amount of work which we have done on this aspect of the problem are that, in general, the indigoid and thioindigoid dyes colour the acrylic fibre to at least the same depth as the cellulosic fibre, whereas the anthraquinone vat dyes colour the cellulosic fibre considerably deeper than the acrylic fibre; there are, however, certain exceptions to this broad classification.

The results of this work are presented in the hope that they will be of sufficient interest to the dyeing and printing industry to warrant further development, as the advantages of the successful application of such a technique on a large scale would appear to offer considerable attractions in the processing and handling of these materials.

* * *

The author wishes to express his thanks to his colleagues in the Technical Service Division of Associated Chemical Companies (Sales) Ltd and to the technical staff of the research laboratories of Courtaulds Ltd for collaboration in the research work, and to the staff of the processing works of Courtaulds Ltd for assistance in carrying out bulk padding trials.

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ASSOCIATED CHEMICAL COMPANIES (SALES) LTD
BROTHERTON HOUSE
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(*MS. received 6th September 1961*)

Discussion

Mr. H. B. HALLOWS: Could leuco esters of vat dyes be used for the production of ground colours in order to overcome some of the difficulties met with single-stage padding with vat dyes? Might this not facilitate the production of solid colours on Courtelle–cotton?

Mr. HANNAY: We did not examine the leuco esters of vat dyes. It is possible that these could be applied by a pad–steam process but, in general, they are still much more expensive to use, particularly for medium and full depths, than the ordinary vat dyes. For this reason the work

described in the paper was confined to the evolution of a suitable technique for the application of vat dyes as such to acrylic fibres and their blends.

Mr. F. W. BELL: Did the authors experience contamination of the reducing bath by the resist, particularly in prolonged runs?

Mr. HANNAY: In our work we did not experience contamination of the reducing bath by the resist, but so far we have had no experience of prolonged runs. It is felt that the problem of contamination could be avoided fairly easily by the design of a suitable padding mangle which had a feeding box of comparatively small liquor content, so that there would be a continuous feed-in of fresh liquor. This problem is one which arises in other padding applications and, generally speaking, does not present great practical difficulties.

Dr. A. WÜRZ: When we were studying the printing of acrylic fibres with basic dyes we wished to reduce the steaming time necessary to develop the colour. With this object in view we developed an agent, Glyecin PFD, which might be of interest for certain acrylic mixtures, e.g. Courtelle–viscose rayon, when printing with selected vat dyes. Glyecin PFD has not, however, shown any special advantages when applied in normal dyeing processes.

Mr. HANNAY: We thank Dr. Würz for his suggestion that the product Glyecin PFD might offer advantages in the application of basic dyes as illuminating colours in producing coloured resists by this process, and will certainly be pleased to carry out experiments to test this (see later).

Mr. HANNAY*: The problem of producing coloured resists under vat dyes by this particular technique is complicated because several factors have to be taken into consideration. As these have not been mentioned in any detail in the paper it is felt that some further statement of these difficulties would be of value. In the production of a coloured resist the following points must be borne in mind—

(*a*) The dye used must be resistant to the reducing action of the alkaline sulphoxylates used for fixing the vat dye, which immediately restricts the number of possible dyes to a rather limited range.

(*b*) When blends are being processed, the dyes used must be capable of being fixed both on the acrylic fibre and on the cellulosic fibre, which again further limits the choice of suitable dyes.

(*c*) The dye used must be compatible with the cationic resist, which constitutes a further limitation.

A consideration of these three points suggested that basic dyes, which are resistant to the reducing action of sulphoxylates and which are known to have an affinity for acrylic fibres, would be suitable, and experiments were carried out with selected dyes. These experiments threw into relief a further problem, namely, that there was competition for the dye sites in the acrylic fibre between the dye and the cationic resist, with the result that the yield of basic dye on the acrylic fibre was greatly reduced compared with that obtained when no resist was present. In addition, the cationic resist, in conjunction with the alkaline reducing solution through which the material was subsequently padded in the fixing of the vat dye, seemed to act as a catalyst and tended to discharge a number of basic dyes that normally were resistant to the reducing effect of sulphoxylates, with the result that near-white resists were obtained instead of coloured ones. This seems to link up with the known technique of discharging dyes that are difficult to discharge with straight sulphoxylates by the addition of certain cationic agents, e.g. quaternary pyridinium compounds. It was therefore felt that a further possibility should be investigated, namely, the use of resin-fixed pigments, as a number of these have been used for producing coloured discharges on dyed grounds on cellulosic fibres with reasonable success. Several suitable pigment-printing compositions were studied and it was found that, although the dyes themselves were not destroyed in the process, the resin binders had affinity for the vat-dye ground, with the result that the resist effect was spoiled.

The above results demonstrate how complicated is the problem of coloured resists; we have not yet been able to overcome the difficulties experienced. In spite of this it is possible to obtain multi-coloured prints by using the white resist in conjunction with ordinary vat dyes printed on top of the ground colour. Such a technique will, of course, be applicable only to pale and medium ground depths where the print-on colour will lift well above the ground.

Since the paper was presented we have carried out some experiments using Glyecin PFD and these have shown that this product, being non-ionic, will not in itself give a resist under the vat-dye ground, and that in order to obtain a white resist it will still be necessary to use a cationic product, which still leaves us with the problem of the competition between the resist and the dye for the dye sites on the acrylic fibre. Work is still continuing in order to determine whether the use of Glyecin PFD will enable better fixation of the basic dye to be obtained. It must also be borne in mind that basic dyes will only fix on the acrylic fibres and that in blends with cellulosic fibre some other method will have to be developed to achieve fixation on both fibres, which is the advantage of the pigment-colour technique.

* Communicated

A Study of the Diffusion of Dyes in Polymer Films by a Microdensitometric Technique

R. H. PETERS, J. H. PETROPOULOS, and R. MCGREGOR

The concentration distributions of dye which are established inside polymer films during dyeing have been determined for the following systems: a disperse dye in cellulose acetate and in nylon, a direct dye in cellulose, and an acid dye in nylon. The results have been analysed to give the variation of diffusion coefficient with dye concentration: this information has been correlated with the practical behaviour of these systems and with their thermodynamic properties.

Introduction

Three distinct stages have been recognised [1] in the production of a uniformly dyed textile fibre by dyeing from an aqueous dyebath. In the first stage, the dye molecules are transported to the fibre/water interface by a combination of aqueous diffusion and mechanical stirring or agitation of the dyebath. The dye molecules are then adsorbed on the outer surface of the fibre. The final stage is the diffusion of the dye inside the fibre until the dye concentration is uniform throughout the fibre phase. Any one of these three processes may control the rate of dyeing.

Rates of dyeing have been used in practice to show the wide range of kinetic behaviour which exists among dyes. The data have been described in graphical form or summarised in terms of a suitable parameter. This parameter may be the time the dye takes to reach an exhaustion of 50% of its final or equilibrium value [2] (time of half-dyeing, $t_{\frac{1}{2}}$) or it may be derived by fitting an appropriate equation, e.g. that of the hyperbola [3], to the data. This approach makes no assumptions about the mechanism of dyeing and is purely an empirical description of the process. In many systems, however, the rate at which the dye diffuses within the fibre is the controlling factor and has an important bearing on the penetration and levelling properties of the dye, as well as on the ultimate wash-fastness of the dyeing. For these reasons alone, the diffusion of dyes in textile fibres is worthy of study. An equally compelling reason is found in the possibility of describing the dyeing process in terms of the laws which govern diffusion. Once the assumption can be made that the rate of dyeing is controlled by the rate at which the dye diffuses into the fibre, a basis exists for predicting the behaviour of a given dyeing system. It is customary to define the diffusion coefficient D of a dye within the substrate by applying Fick's first equation, which for unidimensional diffusion is

$$S = -D\frac{\partial C}{\partial x} \qquad \ldots (1)$$

where S = the flux of dye (quantity crossing unit area in unit time), D = diffusion coefficient, and C = concentration at any point x in the substrate.

A second equation is easily derived from the first by considering the rate of accumulation of diffusant in a given element of volume in the substrate. The equation corresponding to Eqn. 1 has the general form

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \qquad \ldots (2)$$

where t = time.

Eqn. 2 may be solved to obtain a function relating the concentration of dye in the substrate to the time and the point in the substrate under consideration. Integration of this solution with respect to distance will give the total quantity of dye on the fibre as a function of time; such a procedure has been carried out by McBain [4] for a plane sheet, and by Hill [5] for cylinders. The resulting equations therefore describe the rate of dyeing in terms of the diffusion coefficient. In arriving at these equations, the concentration of dye at the surface was assumed to be constant. Solutions for the case where the surface concentration changes are more complicated and are not necessary for studies of the manner in which dye diffuses into fibres. In the work discussed here the surface concentration has been maintained constant.

Studies of the diffusion of dyes into fibrous polymers have shown that D may vary with dye concentration, distance or time, and solutions of Eqn. 2 have been obtained for cases where D is a known function of these variables [6]. Usually D is found to be a function of concentration only and, even though the functions of concentration used for D may make D vary over wide limits, the shape of the adsorption/time isotherm is not very sensitive [6] to the manner in which D varies with dye concentration C. Therefore it is normally possible to calculate only one value of the diffusion coefficient from a given adsorption/time isotherm. This single coefficient $\bar{D}$, which is derived from the experimental adsorption/time isotherm, is usually known as the apparent or integral diffusion coefficient. It has been shown that the following expression gives a good approximation in many instances to the relation between $\bar{D}$ and the actual diffusion coefficient [6, 7] $D(c)$

$$\bar{D} = \frac{1}{C_\infty - C_0}\int_{C_0}^{C_\infty} D(c)\mathrm{d}C \qquad \ldots (3)$$

where C_0 and C_∞ = concentration of dye in the fibre at zero time and after a very long time of dyeing.

$\bar{D}$ therefore has a value which lies between those corresponding to the initial and final dye concentrations in the substrate. Values of the apparent diffusion coefficient $\bar{D}$ can easily be obtained from experimental time/adsorption isotherms or from times of half-dyeing [8]. This correlation between $t_{\frac{1}{2}}$ and $\bar{D}$ applies only to those systems in which dyeing is controlled by the diffusion of dye into the fibre, and the limitations which are found in the usefulness of the apparent diffusion coefficient $\bar{D}$ as a guide to dyeing behaviour will also apply to the corresponding times of half-dyeing $t_{\frac{1}{2}}$. Nevertheless, the time of half-dyeing has proved to be of use in the classification of dyes into groups of distinctly different dyeing behaviour [9]. On the other hand, although the use of $\bar{D}$ or $t_{\frac{1}{2}}$ as a guide to the selection of dyes for use in mixtures has proved satisfactory for disperse dyes in cellulose acetate, it is rather less satisfactory for direct dyes in cellulose and is least useful for acid dyes on nylon. This may arise from different mechanisms of adsorption and diffusion in these systems, each mechanism being associated with a different relationship between $D(c)$ and dye concentration. The apparent diffusion coefficient $\bar{D}$ may not be sensitive to these differences.

This limitation in the information which the diffusion coefficient can reveal is implicit in Eqn. 3. When the diffusion coefficient $D(c)$ is strongly dependent on concentration, as is true in many dyeing systems, the coefficient $\bar{D}$ may be a completely misleading guide to the behaviour of the dye in the substrate. Any theoretical treatment which is based upon measured values for $\bar{D}$ is potentially much less reliable than one which employs measurements of the actual diffusion coefficient $D(c)$. One of the most informative techniques for studying diffusion requires the measurement of the concentration distributions set up during a normal sorption process. This type of measurement can be analysed to give values for the diffusion coefficient $D(c)$, provided that the experimental conditions are chosen carefully to ensure that the sorption process is controlled by diffusion in the substrate.

The multiple membrane or sandwich experiment of Neale [10, 11] was the first attempt to apply this technique to dyeing studies. In these experiments the dye (Chlorazol Sky Blue FF) was allowed to diffuse for a suitable period into a wad of cellulose sheets and each sheet was analysed for dye. On the assumption that the sheets could be regarded as slices of a solid block, these data enabled a concentration–distance relation to be constructed. Other workers [12] have measured the concentration distributions set up during edge-wise diffusion into polymer films. Edge-wise diffusion is carried out by clamping a polymer film between two smooth stainless steel blocks. The film is cut flush with the edge of the block and immersed in a dyebath. Both these methods require longer times of dyeing than apply in practice and they could not easily detect any abnormalities in the behaviour of the dyes during the earlier stages of dyeing. Further, in the sandwich experiments it is not certain what effect the interfaces between the constituent sheets of the multiple membrane may have on the final result; and with edge-wise diffusion experiments it is not easy to ensure that no dye migrates along the surface of the sheet into which edge-wise diffusion is studied.

On the other hand, any attempt to measure the concentration distributions which are set up during short times of dyeing meets severe experimental difficulties, because the maximum extent of dye penetration will be of the order of 10^{-3} cm. Nevertheless, several workers [13, 14, 15] have developed microdensitometric techniques and have applied them to diffusion studies of this kind. So far the results have not been suitable for a detailed analysis in terms of the theory of diffusion. In the present paper the matter has been studied in further detail and an account is given of some results which have been obtained using this type of technique. The data can then be used to throw light on the mechanisms of diffusion in some typical dyeing systems.

Experimental

The techniques employed in this work have been described in detail elsewhere [16] and will only be given in outline here. Small samples of the polymer film were mounted in stainless steel frames which ensured that dyeing was restricted to a definite area of the faces of each sample. The frames were supported in a well-stirred, infinite dyebath by means of stainless steel wires. The dyeing apparatus consisted of a 1·5-l. flask which carried five necks. The central neck was large enough to enable a stirrer to be introduced; the four smaller necks were used to support the samples in the dyebath and also served as a means of inserting or withdrawing the specimens. This apparatus is shown in Fig. 1. Before being dyed, the samples were immersed for several hours in a blank dyebath which was maintained in a thermostat at the temperature used for dyeing.

The dyeing apparatus was maintained at a constant temperature in a thermostat; each sample

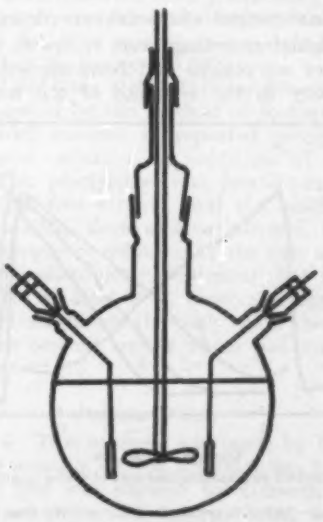

FIG. 1— Dyeing apparatus

was inserted and dyed for a definite period. After dyeing, the samples were removed from the dye-bath, rinsed with jets of ice-cold water, blotted to remove surplus moisture, and withdrawn from their frames. The moist films were then stored in ethanol at −75°C until required for freeze-drying. This drying process was carried out at a temperature between −6 and −10°C by subjecting the films to a pressure of 10^{-2}–10^{-3} mm of mercury. After drying, the dyed films were conditioned in the laboratory and then embedded in an Araldite epoxy resin. Transverse cross-sections were cut from the embedded films with the aid of a microtome. The success of this technique depends upon the quality of the cross-sections; the precautions that must be taken to ensure reliable results have been discussed in detail by the present authors [16], as well as by others [17, 18].

The cross-sections were mounted on microscope slides in a medium of suitable refractive index and scanned with the microdensitometer in order to obtain a curve showing the variation of the optical density with the distance inside the film. The microdensitometer supplied by Joyce, Loebl and Co. Ltd., of Newcastle upon Tyne, had been extensively modified by the authors for this work. It is essential in this kind of work to calibrate the performance of the instrument against known standards. The precautions taken, and the methods of calibration found to be necessary, have been discussed in the paper referred to earlier [16]. In general, the recorded optical density distributions from good cross-sections are characterised by the following features— the section edges are defined by steep optical density gradients and the recordings from opposite sides of the same cross-section are superimposable. Any recordings in which these conditions are not satisfied have been rejected. Fig. 2 shows some recorded profiles in which these conditions were satisfied, curves A and B being recorded at opposite sides of the same cross-section. The dye in this instance was Chlorazol Sky Blue FF and the substrate Cellophane sheet.

PRESENTATION AND ANALYSIS OF DATA

The original recordings were re-drawn on graph paper after corrections had been applied for any non-linearity in the response of the instrument when recording the optical density distribution inside the specimen. In addition, it was occasionally necessary to correct the values of the distance coordinate x for the fact that in some systems diffusion took place into a water-swollen polymer sheet, whereas the optical density distributions were measured on dry cross-sections of the sheet. The constancy of the optical density as obtained by extrapolation of each corrected recording, or profile, to the specimen edge was determined and, after any necessary correction had been made for variations of section thickness, this measurement showed the constancy of the surface concentration during dyeing. Under good cutting conditions, the section thickness was quite reproducible and no correction was necessary. If the surface concentration had been shown to be constant during dyeing, each of the profiles was further corrected to give unit optical density (in arbitrary units recorded by the instrument) at the specimen edge and these optical density profiles, after any necessary corrections for deviations from the Lambert–Beer Law, were plotted on a common graph, as shown in Fig. 3. The final profile for each time of dyeing was the mean of several measurements on different sections [16].

It was then necessary to transform the results. The graphs in Fig. 3 may be put on a single curve by dividing the abscissae by the square root of the time, or preferably by plotting against a new

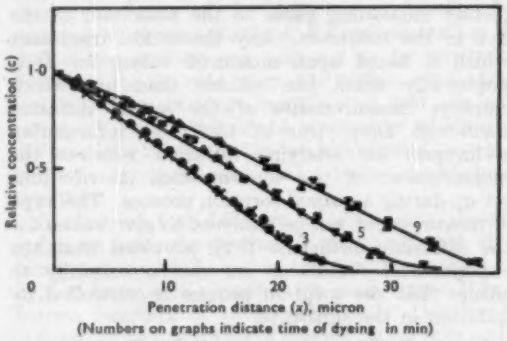

FIG. 3— Diffusion of Chlorazol Sky Blue FF in Cellophane

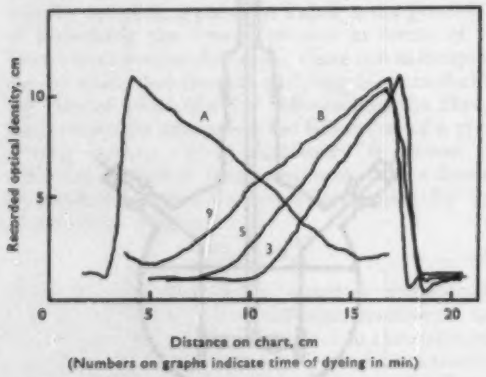

FIG. 2— Diffusion profiles for Chlorazol Sky Blue FF in Cellophane

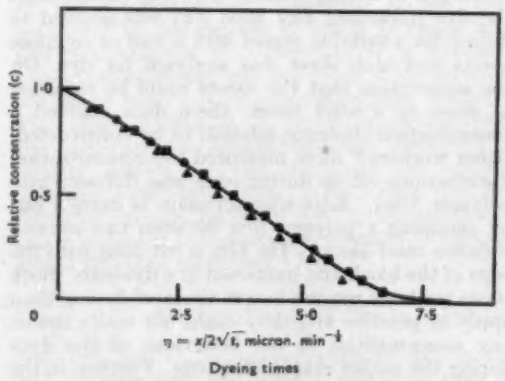

FIG. 4— Diffusion of Chlorazol Sky Blue FF in Cellophane

variable $\eta = x/2\sqrt{t}$ (Fig. 4). The diffusion coefficient may best be obtained from this curve by analysis using Matano's method [16, 18]. This type of plot acts as an additional check on the accuracy of the data, since all results should, within experimental error, fall on a single curve. This is a sensitive test of the adherence of the system to the mathematical model of diffusion from a constant surface concentration into a semi-infinite plane sheet. The most representative smooth curve was drawn through the experimental points on the graph of relative concentration c against $\eta = x/2\sqrt{t}$, where $c = C/C_\infty$ and is numerically equal to the relative optical density. C represents the dye concentration at a point x units distant from the surface at a time t, and C_∞ represents the surface concentration of dye in the film and is assumed to be equal to the dye adsorption at equilibrium (after a very long or almost infinite period of time). The diffusion coefficient/concentration relation was obtained from the experimental results by means of Eqn. 4 [19], which is readily derived from Eqn. 2.

$$D(c)_{(c=c_1)} = -2\left(\frac{d\eta}{dc}\right)_{(c=c_1)} \int_0^{c_1} \eta \cdot dc \qquad \ldots (4)$$

All the terms on the right-hand side of Eqn. 4 can be obtained from the final graph of relative concentration (c) versus $\eta = x/2\sqrt{t}$, and the value of the diffusion coefficient $D(c)$ at any relative dye concentration c_1 may be determined by graphical integration.

Where there is any doubt about the adherence of the system to the mathematical model mentioned earlier, an additional check is available. This consists in measuring the dye sorbed per unit weight of polymer film when a separate batch of specimens is dyed under the conditions used in obtaining the specimens for microdensitometry. When diffusion occurs into a semi-infinite plane sheet (initially free from dye) from a constant surface concentration C_1, the amount of dye M_t taken up by the sheet at time t is given [19] by the equation $M_t = 2C_1\sqrt{Dt/\pi}$. The initial stages of diffusion into a finite plane sheet of polymer correspond to diffusion into a semi-infinite medium; therefore, if C_1 and D are constant, $M_t \propto \sqrt{t}$. If C_1 is dependent on t, this simple proportionality between M_t and $\sqrt{t}$ is not observed. If D is a function of x or of t, this simple proportionality between M_t and $\sqrt{t}$ again disappears [19]. When D depends upon dye concentration C but not explicitly upon any other variable, M_t is again proportional to $\sqrt{t}$ [19]. Therefore if the dye sorption per unit weight of film is plotted against the square root of the time of dyeing, the experimental points should fall, within experimental error, about a straight line through the origin. If they do not, the system is behaving abnormally. If they do satisfy this condition, valuable confirmation is provided that the diffusion coefficient is not a function of time or distance, but of concentration only; it is also implied that the diffusion occurs from a constant surface concentration and that the plane sheet of film may be regarded as semi-infinite during the diffusion process. Fig. 5

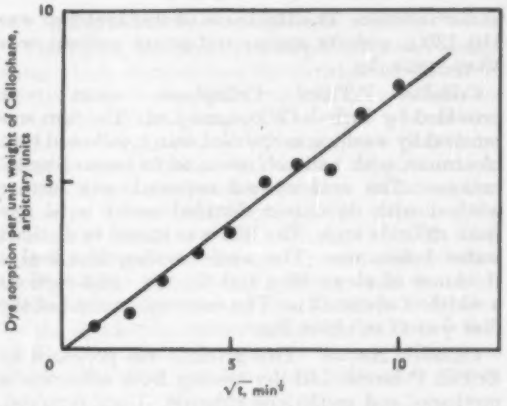

FIG. 5— Rate of dyeing measurements for Chlorazol Sky Blue FF in Cellophane

represents measurements of the uptake of Chlorazol Sky Blue FF at 50°C by Cellophane sheet in presence of 5 g/l. salt, and the results satisfy the conditions already mentioned.

MATERIALS

Dyes

Duranol Red 2B (C.I. Disperse Red 15) Commercial dye was treated with boiling distilled water and the suspension filtered hot. This treatment was repeated five times to remove most of the dispersing agent. The product was dried at 70°C and Soxhlet-extracted with acetone. Recrystallisation of the extract from acetone gave a pure product (m.p. 216°C (uncorr.)) which had the composition—

Found: C, 70·3% ; H, 3·8%; N, 5·6%
$C_{14}H_9O_3N$ requires: C, 70·28%; H, 3·8%; N, 5·8%

Chromatography by several methods failed to show the presence of any isomers.

Naphthalene Scarlet 4R (C.I. Acid Red 18) The commercial dye was recrystallised from aqueous alcohol until samples gave a constant extinction coefficient when dissolved in 20% aqueous pyridine. Chromatography revealed no isomers, and titration of the free dye acid against standard alkali indicated that the purity was 99%.

Chlorazol Sky Blue FF (C.I. Direct Blue 1) This dye was purified by the method of Robinson and Mills [18], which consists in repeated precipitation from aqueous solution by addition of sodium acetate. The precipitate was Soxhlet-extracted with aldehyde-free alcohol, and the residue was further crystallised from aqueous alcohol. Sodium analyses on aqueous solutions of the dye, using an E.E.L. flame photometer, indicated that the dye was probably at least 96% pure; and chromatographic analysis showed that only small amounts of isomers were present, one of which was red and of low substantivity.

Polymer Films

Nylon 6.6 This material was made by E. I. du Pont de Nemours & Co. Inc. by extrusion from the melt. The film was purified by extraction with carbon tetrachloride, the solvent being removed

under vacuum. The thickness of this material was 110–130 μ and its amino end-group content was 45 m equiv./kg.

Cellulose P.T.600 Cellophane sheet was provided by British Cellophane Ltd. The film was purified by washing in distilled water, followed by a treatment with hydrochloric acid to remove metal cations. The acid-washed material was further washed with de-ionised distilled water until free from chloride ions. The film was stored in distilled water before use. The water-swollen film had a thickness of about 92 μ and the dry cross-sections a width of about 42 μ. The carboxyl content of the film was 42 m equiv./kg.

Cellulose Acetate This product was prepared by British Celanese Ltd. by casting from solutions in methanol and methylene chloride. Until required, the film was stored in distilled water. The acetyl value of this material was 54·6%, and its thickness was about 50 μ.

Results and Discussion

The failure of measured apparent diffusion coefficients and times of half-dyeing to provide a complete description of the practical behaviour of some of the common dyeing systems appears to arise either from the fact that the dyeing processes concerned are not controlled by the diffusion of the dye within the fibre or from the variation of the actual diffusion coefficient with the dyeing conditions. The manner in which the diffusion coefficient D varies with, e.g., dye concentration and electrolyte concentration is probably intimately connected with the mechanism of diffusion in the substrate. It is therefore necessary to discuss briefly some of the important factors which may control the magnitude of the diffusion coefficient.

A diffusion process can be pictured as arising from random movements of the diffusing molecules, which nevertheless result in the net transport of matter from a region of higher concentration to one of lower concentration [21]. Thus the tendency of any system to increase in entropy is reflected in the levelling-out of concentration inequalities as a result of diffusion. The rate of transport of matter in such a system is directly related to the space gradient of concentration of diffusant molecules, and Fick's first law of diffusion (Eqn. 1), in which the diffusion coefficient D is constant, should be valid. Deviations from Fick's Law, i.e. non-constancy of D, can arise in this model if the concentration C does not represent the actual number of molecules free to diffuse. Thus some of the molecules in the element of volume where the concentration appears to be C units may be adsorbed and immobile in the substrate and therefore not available for diffusion. This possibility has been examined by Standing [22] and by Crank [23], and will be discussed in more detail later. It has been shown by these workers that deviations from Fick's Law occur when the concentration of immobilised molecules is not a linear function of the concentration of free molecules. A further possibility arises from interactions between individual diffusing molecules, e.g. as a result of their being electrically charged, which again affect the randomness of the molecular motions or the number of molecules free to diffuse. This is illustrated by the effect which the quickly diffusing cation has on the diffusion of a dye anion. At low electrolyte concentrations the cation tends to diffuse in advance of the anion and a diffusion potential is set up which accelerates the movement of the dye anion itself. This effect decreases as added electrolyte modifies the interactions of the diffusing particles. The dye will also act as its own screening electrolyte and the diffusion coefficient will show a dependence on dye concentration: Fick's Law will therefore not be obeyed. If dye particles associate to form aggregates, the number of particles free to diffuse will not be given by the bulk concentration of dye and Fick's Law may therefore not be valid.

Another approach is to regard the diffusion as occurring by movement of the molecules under the influence of a force. This force may arise from the gradient of osmotic pressure [24], or of chemical potential [25], which is associated with the concentration gradient in the material. The molecules will acquire a velocity which is such that the resistance of the medium to movement of the molecules is balanced by the driving force, and this velocity will determine the rate of transport of matter in the system. This theme has been developed by several workers [26, 27, 28], but cannot be discussed in detail here. The treatments that have been used show that Fick's Law must be replaced by an equation which, if the gradient of chemical potential be the driving force, takes the form

$$S = D'C \cdot \frac{\mathrm{d}\mu}{\mathrm{d}x} \qquad \ldots\ldots(5)$$

The diffusion coefficient D' may here be regarded as a mobility factor which is related to the resistance which the medium offers to diffusion. If μ in Eqn. 5 be replaced by $\mu_0 + \boldsymbol{R}T \ln a$, (where a = activity of the molecules at concentration C), the equation may be transformed to one which includes the concentration gradient, i.e.

$$\begin{aligned} S &= -D'C\frac{\partial(\mu^\circ + \boldsymbol{R}T\ln a)}{\partial x} \\ &= -D'\boldsymbol{R}T\frac{\partial \ln a}{\partial \ln C}\cdot C\cdot\frac{\partial \ln C}{\partial x} \\ &= -\boldsymbol{R}TD'\left(\frac{\partial \ln a}{\partial \ln C}\right)\cdot\frac{\partial C}{\partial x} \qquad \ldots\ldots(6) \end{aligned}$$

Eqn. 6 is now in the form of Fick's first law with

$$D(c) = \boldsymbol{R}TD'\left(\frac{\partial \ln a}{\partial \ln C}\right) \qquad \ldots\ldots(7)$$

If the system behaves ideally when $C \to 0$, i.e. if $a \to C$ as $C \to 0$; then, as $C \to 0$, $\left(\frac{\partial \ln a}{\partial \ln C}\right) \to 1{\cdot}0$ and

$$\boldsymbol{R}TD' = \underset{(c=0)}{D(c)} = D_0$$

Therefore,

$$D(c) = D_0\left(\frac{\partial \ln a}{\partial \ln C}\right) \qquad \ldots\ldots(8)$$

Alternatively, if the activity a of the diffusing molecules is a measure of the number of molecules

that are free to diffuse at a concentration C, then Eqn. (1) can be re-written as

$$S = -D'' \frac{\partial a}{\partial x} \quad \ldots . (9)$$

and it follows from the assumption of ideal behaviour at infinite dilution that

$$D(c) = D_0 \left(\frac{\partial a}{\partial C}\right) \quad \ldots . (10)$$

Eqn. 8 and 10 are the two thermodynamic alternatives on which discussion of the results will be based.

DURANOL RED 2B IN CELLULOSE ACETATE

In Fig. 6 is drawn the concentration/distance curve which would be expected if the diffusion coefficient was constant, i.e. if Fick's Law was obeyed for the diffusion of dye from a constant surface concentration into a plane sheet

$$C/C_\infty = 1 - \text{erf.}(x/2\sqrt{Dt}) \quad \ldots . (11)$$

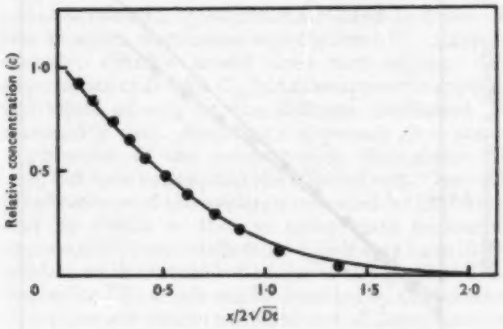

FIG. 6— Diffusion of Duranol Red 2B in cellulose acetate

The agreement between this curve and the experimental points, which were obtained from a profile recorded by the microdensitometer, is satisfactory [29]. This result could mean that any variations in the thermodynamic terms in Eqn. 8 and 10 are exactly compensated by changes in D_0 as a result of, e.g., plasticisation effects. This is unlikely and the constancy of D is presumably a consequence of the thermodynamic ideality of the system. This view is compatible with the evidence provided by equilibrium dyeing studies [29, 30, 31]. The success which dyeing theory has had in predicting the behaviour of disperse dyes in cellulose acetate fibre is therefore a consequence of the constancy of D and of the ideality of the system.

DURANOL RED 2B IN NYLON 6.6

It has been established that the diffusion of this dye into nylon 6.6 from a well stirred solution in iso-octane saturated with water shows only slight deviations from Fick's Law over a considerable part of the concentration range studied [32]. This finding is explained in the same manner as for the diffusion of this dye in cellulose acetate, and is obviously relevant to the better levelling properties of the disperse dyes on nylon as compared with the acid dyes.

NAPHTHALENE SCARLET 4R IN NYLON 6.6

The nylon film was dyed at pH 3·2 under conditions which ensured that the surface concentration of dye was almost that required to saturate the terminal amino groups. The dye was chosen because several workers [34, 35] have shown that under certain conditions there is an approximately stoichiometric relationship between its adsorption by nylon 6.6 and the amino-group content of the fibre. The diffusion profiles are shown in Fig. 7(*a*), and the diffusion coefficient–concentration relation in Fig. 7(*b*). This $D(c)/C$ relation could be interpreted either as a marked plasticisation of the fibre by the dye as the concentration of dye rises (effect on D_0) or as marked departure of the system from ideal behaviour in the thermodynamic sense.

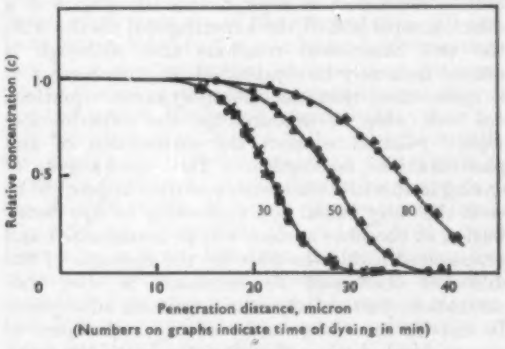

FIG. 7(*a*)— Diffusion of Naphthalene Scarlet 4R in nylon

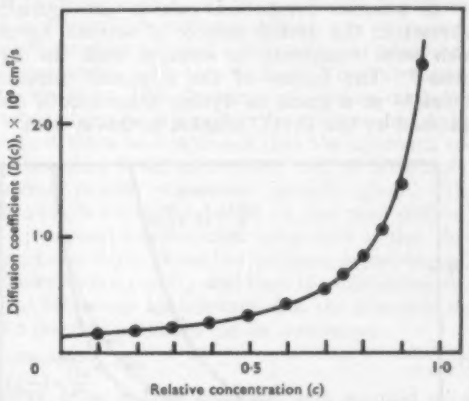

FIG. 7(*b*)— Relation between diffusion coefficient and concentration (Naphthalene Scarlet 4R in nylon)

There is little evidence to support a plasticisation mechanism and it seems likely that any changes in the fibre structure will have occurred before dyeing by virtue of the adsorption of water when the fibre was immersed in the blank dyebath. The $D(c)/C$ relationship obtained is compatible with the variation in the thermodynamic terms which would arise if the dye molecules were adsorbed on fixed sites, e.g. the charged amino end-groups. This is tantamount to the substitution of the activity function used in adsorption experiments into Eqn. 8 and 10. On the basis that an anion of

basicity Z occupies Z sites, the activity of the dye anion has been calculated to be given by the expression [36]

$$a = \frac{1}{Z} \cdot \frac{\theta}{1-\theta} \quad \ldots . (12)$$

where $\theta = C/S$ = fractional saturation of the sites.

It follows from Eqn. 8, 10, and 12 that two possibilities must be considered—

$$\text{from Eqn. 8} \qquad D(c) = D_0\left(\frac{1}{1-\theta}\right) \quad \ldots . (13)$$

$$\text{from Eqn. 10} \qquad D(c) = D_0\left(\frac{1}{1-\theta}\right)^2 \quad \ldots . (14)$$

From the results given in Fig. 7(*b*) an opportunity now exists for distinguishing between the possibilities expressed in Eqn. 8 and 10. Fig. 8 is a direct comparison of the experimental results with the two theoretical relations and, although it cannot definitely be established which is correct, it is quite clear that the thermodynamic equations are well able to account for the experimental $D(c)/C$ relation without the assumption of any plasticisation mechanism. The mechanism of dyeing in this substrate with acid dyes appears to be such that any initial non-uniformity of dye distribution at the fibre surface will be accentuated and propagated inside the fibre by the response of the diffusion coefficient to increases in dye concentration, particularly near saturation adsorption. It can be seen why many of the techniques to ensure level dyeing of nylon are based on some restriction of the initial dye adsorption, e.g. by the use of anionic compounds which are initially adsorbed on the dyeing sites or of cationic agents which form complexes in solution with the dye anions [37]. The failure of the apparent diffusion coefficient as a guide to dyeing behaviour is also explained by the $D(c)/C$ relation in this system.

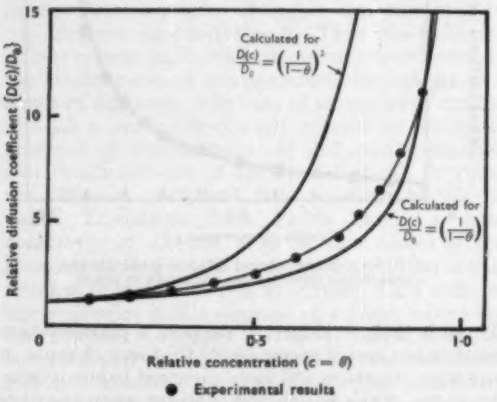

FIG. 8— Test of thermodynamic equations (Naphthalene Scarlet 4R in nylon)

CHLORAZOL SKY BLUE FF IN P.T.600 CELLOPHANE

The diffusion profiles obtained from samples dyed at 90°C from a dyebath containing 1 g/l. Chlorazol Sky Blue FF and 5 g/l. sodium chloride are shown in Fig. 3 and 4. The corresponding $D(c)/C$ relation is shown in Fig. 9: it can be seen that a linear relation of the type $D(c) = D_0(1+\alpha c)$ can be applied to the results, but that there are two ways of doing this. The initial slope of the experimental results (line A) corresponds to the relation $D(c) = D_0(1+10{\cdot}7\,c)$, whereas the line B, fitted by the method of least squares to all the experimental points, corresponds to the expression $D(c) = D_0(1+5{\cdot}5\,c)$. It is interesting to compare the present result with that obtained by Neale [10] in his multiple-membrane experiment as re-analysed by Crank [11]. When the two equations just given are expressed in terms of the actual dye concentration C (in grams of dye per 100 grams of dry cellulose) instead of the relative concentration c, the parameter β in the corresponding equation

$$D(c) = D_0(1 + \beta C)$$

can be calculated.

Table I is a comparison of the present result with that of Neale [10] as re-analysed by Crank [11].

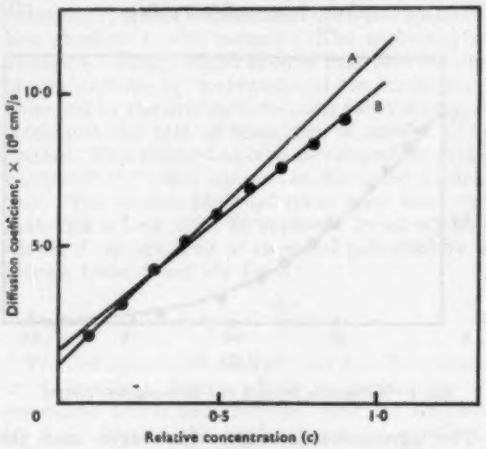

FIG. 9— Relation between diffusion coefficient and concentration for Chlorazol Sky Blue FF in Cellophane

TABLE I

D_0 (cm²/s × 10^{-6})	β	Comments
1·50	1·60	Line B in Fig. 9
1·00	3·00	Line A in Fig. 9
0·80	1·94	Crank's re-analysis of Neale's result

The difference in the D_0 values obtained by Neale and by the present authors is easily accounted for by the fact that the properties of Cellophane sheet may be somewhat different nowadays. In any event the difference is not alarming, and even Crank and Neale's value for the parameter β could easily be obtained from the present results by fitting a straight line intermediate between lines A and B in Fig. 9.

Thus there is almost quantitative agreement between the present results and those obtained by an entirely different technique. An explanation must now be found for this linear relationship. Standing [22] and Crank [19] have shown that it can occur if the dye in the cellulose is considered to be in part adsorbed and immobilised (concentration

C_A) and in part free to diffuse (concentration C_i) in "pores" in the substrate. It can be shown on these assumptions that the measured diffusion coefficient $D(c)$ is related to the diffusion coefficient D_i for "pore" diffusion by the expression

$$D(c) = \alpha D_i \frac{dC_i}{dC_A} \quad \ldots.(15)$$

where α is the fractional volume occupied by the pores of the cellulose, or, if diffusion of the adsorbed dye can occur with a diffusion coefficient D_A

$$D(c) = \alpha D_i \frac{dC_i}{dC_A} + D_A \quad \ldots.(16)$$

On Standing's model, C_i is equal to the dyebath concentration C_s which would be in equilibrium with the concentration C_A of adsorbed dye, so that $\frac{dC_i}{dC_A}$ becomes equal to the reciprocal gradient of the external adsorption isotherm. On Crank's model $\frac{dC_i}{dC_A}$ is constant and C_i is related to the dyebath concentration C_s by equations related to those of the Donnan membrane equilibrium [1, 23]. Consequently, Crank's model does not explain the dependence of D upon C_A, but does appear to explain the effect of salt on the diffusion coefficient D reasonably well. Standing's approach gives some explanation of the concentration dependence of $D(c)$ but does not explain the effect of salt. One real disadvantage of the evidence provided by Standing and by Crank is that it relies upon measured apparent diffusion coefficients which may have little relation to the actual behaviour of the system. The values for $D(c)$ which can be provided by the present technique will enable a critical test of these theories to be made. At the moment a linear dependence of $D(c)$ upon C_A is explained on Standing's model by the expression

$$\frac{dC_i}{dC_A} = kC_A \quad \ldots.(17)$$

which on integration gives

$$C_i = \frac{k}{2} C_A^2 + K' \quad \ldots.(18)$$

Since, when $C_i = 0, C_A = 0; K' = 0$

$$\text{and} \quad C_i = \frac{k}{2} C_A^2 \quad \ldots.(19)$$

$$\text{then} \quad C_A = \left(\frac{2}{k}\right)^{0.5} C_i^{0.5} \quad \ldots.(20)$$

Thus a linear dependence of D upon C_A is explained by an internal partition of dye of the Freundlich type where the exponent is 0·5. It appears that C_i should be calculated from C_s by applying the principle of the Donnan membrane equilibrium, since this will enable the effect of salt and of dye concentration to be taken into account at the same time [1]. The problem has been approached in a similar manner by Heritage [38], who postulates that a Donnan membrane equilibrium exists between the dye in the dyebath and the dye which is free to diffuse in the fibre, and that a Langmuir adsorption isotherm exists between the adsorbed dye and the dye which is free to diffuse in the cellulose. On this basis, the concentration dependence of the diffusion coefficient is explained by the equation [38]

$$D(c) = D_i \exp\left(\frac{\Delta G}{RT}\right)\left\{1 + 2\frac{C_A}{C_{sat}}\right\} \Big/ C_{sat}$$

which reduces to the form

$$D(c) = D_0\left(1 + \left[\frac{2}{C_{sat}}\right] C_A\right) \quad \ldots.(21)$$

In this expression C_{sat} represents the saturation adsorption for the Langmuir isotherm, and it is assumed that $C_A \ll C_{sat}$. Eqn. 21 was put forward as an explanation of the linear variation of $D(c)$ with C_A in Neale's experiment and was stated to explain adequately Heritage's own results with Chrysophenine G. Unfortunately, Heritage's diffusion coefficients are of the integral type ($\bar{D}$) and have been related to the maximum dye concentration for each experiment, whereas they are more closely related to the mean concentration employed. For this reason, Heritage's experimental values for β in the expression $D(c) = D_0(1+\beta C_A)$ have little real significance and the agreement with theory is probably fortuitous. It can further be shown that for Neale's results it would be necessary, since $\beta = 1{\cdot}94$, to assume that $C_{sat} = 1{\cdot}03$ g/100 g, and this value is much less than the equilibrium dye uptake of 3 g/100 g in this experiment. It cannot be said, therefore, that an internal Langmuir adsorption isotherm provides an adequate explanation of the linear $D(c)/C$ relationship.

Holmes has shown [39] that the internal isotherm for Chrysophenine G in cotton cellulose corresponds to a Freundlich isotherm where the exponent is approximately 0·5, and a linear $D(c)/C$ relationship is compatible with this finding. The extension of this result to other dyes and to cellulose containing carboxyl groups is a matter for conjecture. At this stage it must be mentioned that the approach used by Standing is an alternative way of utilising the thermodynamic equations already given. Thus Standing's assumption that D_i (for pore diffusion) is a constant implies ideal behaviour of the "free" dye, i.e. $a_i = C_i$. Since the isotherm is non-linear, it follows that $a_A \neq C_A$ and that the deviations from ideal behaviour are attributed to the adsorbed dye. The internal partition can be written as

$$a_A = k^0 a_i \quad \ldots.(23)$$

where k^0 is a true constant and a_A and a_i are activities. Since $a_i = C_i$, then $a_A = k^0 c_i$

$$\text{and} \quad \frac{da_A}{dC_A} = k^0 \frac{dC_i}{dC_A} \text{ (compare with Eqn. 15)} \quad \ldots.(24)$$

It is clear therefore that the treatment given by Standing is an attempt to account for the diffusion behaviour by applying thermodynamic corrections obtained from adsorption measurements. This has already been recognised by Crank [40] and deserves emphasis here. It seems to us that the diffusion behaviour in this system is intermediate between those observed in the other two systems mentioned in this paper, viz. disperse dyes on cellulose acetate, and acid dyes on nylon. This implies a mechanism of adsorption which is also of an

intermediate type and which does not correspond to that of Langmuir. The formulation as a Freundlich isotherm is without theoretical basis and it appears that the explanation of this linear $D(c)/C$ relationship will not be simple. At best it may not be possible to do more than show that the thermodynamic corrections which are obtainable from calculated internal isotherms are in agreement with the diffusion results. Work on these lines has already been started.

Conclusions

The manner in which the diffusion coefficient varies with dye concentration in the systems studied in this paper has been compared with the behaviour predicted from the two equations

$$D(c) = D_0\left(\frac{\partial \ln a}{\partial \ln c}\right)$$

and

$$D(c) = D_0\left(\frac{\partial a}{\partial c}\right)$$

The disperse dyes appear to dye cellulose acetate by a process of solution of the dye in the fibre, and since the partition of dye between dyebath and fibre is linear in this system it appears that the dye in the fibre behaves ideally. Both equations reduce to the form $D(c) = D_0 =$ constant under these conditions, and in agreement with these predictions the diffusion of Duranol Red 2B in cellulose acetate has been found to conform to Fick's Law.

The diffusion of Naphthalene Scarlet 4R in nylon 6.6 has been found to be strongly dependent on dye concentration in a manner which can be explained to a first approximation by either of the two equations without assuming any plasticisation or other effects. This concentration dependence of $D(c)$ has been shown to be a natural consequence of the mechanism of dyeing in this substrate, which can be treated as a process of adsorption of dye on to fixed sites in the fibre. This behaviour is in marked contrast to that of the disperse dye Duranol Red 2B in the same substrate, which conforms to Fick's Law and presumably implies a similar mechanism of adsorption to that for disperse dyes in cellulose acetate.

The diffusion coefficient of Chlorazol Sky Blue FF in cellulose shows an approximately linear dependence on dye concentration: this behaviour can be regarded as intermediate between that for the disperse dye in cellulose acetate and that for the acid dye in nylon. This variation of $D(c)$ with dye concentration can probably be explained in thermodynamic terms, i.e. by equations of the type already used, but this requires the calculation of the correction terms $\left(\frac{\partial a}{\partial C}\right)$ and $\left(\frac{\partial \ln a}{\partial \ln C}\right)$ from equilibrium dyeing studies.

The different behaviour of each of these systems provides an explanation of the observation that D and $t_{\frac{1}{2}}$ are useful guides in the dyeing of cellulose acetate with disperse dyes but are less useful in the dyeing of cellulose with direct dyes and least useful as an indication of the behaviour of acid dyes in nylon. Some of the precautions which are taken to ensure the level dyeing of polyamide fibres with acid dyes can be explained in the light of the observed diffusion behaviour of this system.

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References

[1] Vickerstaff, *The Physical Chemistry of Dyeing* (London: Oliver and Boyd 1954).
[2] Boulton and Reading, J.S.D.C., **50**, 381 (1934).
[3] Vickerstaff, *ibid.*, **59**, 92 (1943).
[4] McBain, *Z. phys. Chem.*, **68**, 471 (1909).
[5] Hill, *Proc. Roy. Soc. B*, **104**, 39 (1928).
[6] Crank and Henry, *Trans. Faraday Soc.*, **45**, 636, 1119 (1949).
[7] Standing, Willis, and Warwicker, *J. Textile Inst.*, **38**, T335 (1947).
[8] Kilby, J.S.D.C., **76**, 479 (1960).
[9] Boulton, *ibid.*, **60**, 5 (1944).
[10] Garvie and Neale, *Trans. Faraday Soc.*, **34**, 335 (1938).
[11] Crank, *Phil. Mag.*, **39**, 362 (1948); cf. J.S.D.C., **64**, 386 (1948).
[12] Warwicker, Private communication.
[13] Jelley and Pontius, *J. Phot. Sci.*, **2**, 15 (1954).
[14] Olofsson, *Medd. Svensk Textilforskninginst.*, 29 (1953).
[15] Luck, *Melliand Textilber.*, **36**, 927, 1028, 1267 (1955).
[16] Peters, Petropoulos, and McGregor, forthcoming publication.
[17] Oster and Pollister, *Physical Techniques in Biological Research*, Vol. 3 (New York: Academic Press 1956).
[18] Hillier and Gattner, *J. Applied Phys.*, **21**, 889 (1950).
[19] Crank, *The Mathematics of Diffusion* (Oxford: Clarendon Press 1956).
[20] Robinson and Mills, *Proc. Roy. Soc. A*, **131**, 576 (1931).
[21] Einstein, *Z. Elektrochemie*, **14**, 235 (1908).
[22] Standing, Warwicker, and Willis, *J. Textile Inst.*, **38**, T335 (1947).
[23] Crank, J.S.D.C., **63**, 412 (1947).
[24] Nernst, *Z. physik Chem.*, **2**, 613 (1888).
[25] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).
[26] Babbitt, *Canadian J. Phys.*, **29**, 427 (1951).
[27] Onsager, *Annals New York Acad. Sci.*, **46**, Art 5, 241 (1945).
[28] Crank and Hartley, *Trans. Faraday Soc.*, **45**, 801 (1949).
[29] Peters and Petropoulos, *Bull. Inst. Text. France*, No. 84, 49 (1959).
[30] Azad, Johnson, and Peters, forthcoming publication.
[31] Vickerstaff, Ref. 1, p. 336.
[32] Peters, Ramachandran, and McGregor, unpublished work.
[33] Peters, Petropoulos, and McGregor, forthcoming publication.
[34] Peters, J.S.D.C., **61**, 95 (1945).
[35] Palmer, *J. Textile Inst.*, **49**, T33 (1958).
[36] Atherton, Downey, and Peters, *Text. Research J.*, **25**, 977 (1955).
[37] Bittles, Brooks, Iannarone, and Landerl, *Amer. Dyestuff Rep.*, **47**, 183, 194 (1957).
[38] Heritage, *Trans. Faraday Soc.*, **54**, 1902 (1958).
[39] Holmes, *ibid.*, **54**, 1172 (1958).
[40] Crank, *Symposium on Fibrous Proteins*, p. 115 (Bradford: Society of Dyers and Colourists 1946).

Discussion

Dr. W. BECKMANN: Your experimental techniques seem to be rather difficult. It would be much easier to employ the sandwich technique, but this can be done only if the dye concentrations of the single films are equal on the surfaces in contact with one another. Did you do any experiments to find out whether this is the case?

Professor PETERS: A comparison of our own results with the result of an experiment carried out by Neale, who used the sandwich technique, has

been made in our paper (Table I). The agreement between the two methods suggests that the interfaces between the constituent sheets of the sandwich do not cause any perturbations of the diffusion process in this system; this may not be so for other substrates and other dyes. Dr. Patterson has pointed out that an interesting variation of the sandwich technique has been developed by Sekido of the Tokyo Institute of Technology and applied to a number of dyeing systems.

The analysis of these results was made by a technique which gave a mean diffusion coefficient for the concentration range of dye employed; unless at least ten layers of the sandwich are penetrated by the dye it is difficult to construct from the results a diffusion profile which can be analysed by Matano's method. A long time of dyeing is therefore required unless extremely thin films are used. Some of the more interesting and perplexing aspects of dyeing kinetics are associated with the initial stages of the process; these effects cannot be detected by the sandwich technique.

Mr. H. R. HADFIELD: Have the authors examined the application of neutral-dyeing acid dyes to nylon from acid dyebaths and from neutral dyebaths? If this work has been carried out do the results indicate a radically different dyeing mechanism?

Professor PETERS: This system is of great interest and we intend to study it in the near future.

Dr. D. PATTERSON: I should like to congratulate the authors on the progress they have made in this difficult technique. The Becke line effect, which is troublesome in microdensitometer work, can sometimes be eliminated by the use of plane-polarised light and the accurate matching of the refractive index of the substrate (in a given direction if it is birefringent) by a mounting medium (Patterson and Ward, *Trans. Faraday Soc.*, **53**, 1516 (1957)). Have the authors considered using this method to minimise the difficulties at the beginning of the scan when the edge of the specimen is in the field of view?

Professor PETERS: It is, of course, impossible to eliminate the Becke line effects with a highly birefringent material such as Terylene unless plane-polarised light is used. We are carrying out experiments with the microdensitometer using polaroid filters and accurate matching of the refractive index of the substrate in plane-polarised light, but so far we have had little success because the polaroid filters reduce the light intensity reaching the photomultiplier to an unacceptable level. There are also other problems associated with dichroism of the dyed material and, as Mr. Hadfield has mentioned, the effect of structural variations in the films which might be emphasised by using polarised light.

Mr. J. BOULTON: The technique used for measuring concentration gradients in dyed film is clearly sound, but would seem to be very slow and to require great pains. In early work on dye diffusion, use was made of a flat film held between very finely ground flat surfaces, and the course of diffusion into the exposed edge was observed by separating the clamp–film sandwich and examining the advancing dye boundary. This extremely simple technique produced useful results, and I should like the authors' view as to whether some such simple method was not still available to them.

Professor PETERS: The experimental technique which Mr. Boulton mentions is very useful: some excellent results have been obtained in this way by Warwicker [12], who carried out a detailed examination of the diffusion of Chrysophenine G into never-dried Cellophane sheet, and was able to derive diffusion coefficient–concentration relationships from his results. The only disadvantages are that a long time of dyeing is required, which prevents the detection of abnormalities during the early part of the process; that the process is not readily adapted to a study of steady-state diffusion; and that unless very thin films are used the range of dye concentrations that can be employed is limited. In many other ways the technique has much to recommend it and we shall probably use it to study diffusion processes which we have found to behave abnormally during the time scale of a normal dyeing process.

Mr. BOULTON: The authors have worked, for good reasons, in an infinite dyebath. A good deal of mathematical treatment has been given in the last ten years to problems of diffusion and one wonders if the authors have found it still impossible to interpret measurements made in a finite dyebath. The results of such studies might throw useful light on the dyeing process as met with in practice.

Professor PETERS: Studies of diffusion from a finite dyebath are a logical development of the work which we have already done and as soon as the phenomena associated with the infinite dyebath have been properly characterised we shall be in a position to do this kind of work. There would be little difficulty in obtaining results of qualitative interest: a detailed analysis of the diffusion profiles would be more difficult because of the combined influence of the variable boundary conditions and the concentration-dependence of the diffusion coefficient on the profiles themselves. This difficulty might necessitate the use of modern computer techniques in the analysis of the results.

Mr. I. GAILEY: Professor Peters has shown that diffusion data fall into two groups, viz.

Type A, which he associates with non-ionic dyeing systems

Type B, which he associates with ionic dyeing systems,

and that the dyeing behaviour of cellulose lies between these two extreme types, i.e. cellulose displays a combination of non-ionic and ionic characteristics.

In the experiments described in this paper, the carboxyl-group contents of the cellulose specimens were measured. Have different positions between the two extreme types A and B been found for different celluloses and has any relationship been found between these intermediate positions and the carboxyl-group contents of these cellulose samples?

Dr. MCGREGOR: We have not yet made a systematic study of the influence of the carboxyl content of the cellulose films on the diffusion behaviour of direct dyes. Presumably the factor

of importance here is the number of carboxyl groups present that are fully dissociated, and this will vary with factors such as the pH of the dyebath and the total carboxyl content of the material. We have used our own measurements of the dissociation constant of the carboxyl groups in these films to calculate the "internal isotherm" according to an extension of Holmes's method[39], and it is possible to find some correlation between the nature of this isotherm and the observed diffusion behaviour. We would only expect behaviour of type B with an ionic system in which a dye ion is attracted to oppositely charged groups in the fibre structure, i.e. profiles resembling those obtained with acid dyes on nylon might well be obtained with cellulose which contains carboxyl groups if this material were dyed with a cationic dye.

Dr. W. LUCK*: The interesting results obtained by the authors have been confirmed in experiments that we have carried out on nylon 6. The diffusion of Orange II (C.I. Acid Orange 7) from aqueous solutions into nylon 6 monofilaments has been observed by means of a recording microspectrophotometer. Similar deviations from the normal diffusion curve, as shown in Fig. 7(*a*), were found. The more rapid diffusion observed at high dye concentrations is more pronounced for unstretched monofilaments than for stretched ones. The deviations from the normal diffusion curve were even more marked in the dyeing of Orange II from methanolic solution on nylon 6. On the other hand, the steeper section of the diffusion curve at high concentrations was less pronounced when the dye was applied from a mixture of equal parts of water and methanol. The results indicate that the hydrogen bonds of the fibre are involved in the effect under discussion.

Dr. MCGREGOR*: The results which Dr. Luck has outlined are very interesting, but we should like to have much more information about the measurements themselves before commenting on them in detail. We should like to emphasise that a qualitative consideration of diffusion profiles alone may be misleading. The proper description of the system comes from the diffusion coefficient–concentration relationship, since what appear at first sight to be widely different diffusion profiles may, when analysed, give a similar $D(c)/C$ relation at the lower to medium dye concentrations.

It is in this lower concentration range that our treatment of the data is most applicable. We have assumed no physical restrictions to the upper values of $D(c)$ in our treatment; this is an obvious simplification, and if an increase of order in the substrate places such restrictions on $D(c)$ the diffusion profiles will certainly alter. There must also be in any one dye a certain balance of ionic and non-ionic bonding to the substrate: the more pronounced the non-ionic component, the more the diffusion profiles will tend towards the Fickian profile. For this reason we have chosen Naphthalene Scarlet 4R (C.I. Acid Red 18) as a dye which should be primarily influenced by ionic effects, but we are also carrying out experiments with dyes such as Naphthalene Red J (C.I. Acid Red 88) to investigate other factors. There is no doubt that a complete description of diffusion into nylon will be more complicated than the picture put forward here.

* Communicated

Chairman—Mr. J. BOULTON

A Study of the Dyeing Behaviour of Abraded Wool

H. R. HADFIELD and D. R. LEMIN

A study has been made of the effect of abrasion of wool on the characteristic properties of individual acid dyes on wool fibres. When abrasion takes place before dyeing, the abraded areas dye initially more heavily than the unabraded areas. When abrasion occurs after dyeing, the abraded areas appear to be less heavily dyed, owing to an optical effect caused by fibrillation of the fibres. Rubbing of wool against wool produces an effect identical with that obtained on abrasion by glass-paper or other abrasives. The time required to produce level dyeings on abraded wool varies widely from dye to dye, and the degree of sulphonation of the dye has an important effect. Certain cationic auxiliary agents reduce the time required to produce level dyeings. Apparently, abrasion increases the hydrophilic nature of the fibre surface.

Introduction

The characterisation of unlevelness in wool dyeing is a problem which is presented to dyers and dye manufacturers every day. In piece-dyed material this is often difficult because of the large number of processes which have been encountered before the dyeing operation. In addition to having been scoured as loose wool, a typical woollen cloth will have been piece-scoured, milled, and carbonised before being dyed. Apart from any unlevelness arising from improper application of dye, any of these processes could be the cause of trouble during dyeing.

The literature on the effect of various chemical treatments on wool is voluminous. The effect of acids, alkalis, and oxidising and reducing agents on wool has been the subject of much study, and the effect of such treatments on the dyeing properties of dyes is well known. The relation of faulty dyeing to the chemical damage suffered by the wool during processing has been studied and has resulted in the publication of several papers [1–3].

In spite of all the information available, it had been found, in the examination of faulty piece goods, that it was often impossible to ascertain the precise cause of the fault. It was observed that many of these faults occurred in the heavier woollens which had been milled and carbonised before being dyed. The fault usually consisted of ill-defined warpwise streaks; on examination there would be no evidence of uneven carbonisation, the pH across the width of the material and the residual grease content would be uniform, and yet it would be extremely difficult, if not impossible, to level the material by giving a normal levelling boil.

The possible cause of these faults was first suggested by Parker [4], who presented evidence that they were due to mechanical abrasion during processing. His observations, based on practical dyeing experience, showed that if the material was "bagged" (i.e., sewed selvedge to selvedge) before being wet processed, the protected inside face of the cloth dyed evenly, whereas the exposed outside of the material showed the typical streaky fault. It was suggested that slippage of the top roller in a dolly scouring machine was one of the main factors causing the fault. Since these observations, examination of a large number of unlevel dyeings on wool cloths has shown that the fault was ascribed correctly to abrasion damage. The effect, whilst occurring mainly in heavier woollens, has also been observed on knitted jersey fabrics.

Jenkins and Keels [5] examined the effect of abrasion on the dyeing characteristics of cotton and found that the abraded areas of knitted cotton material dyed more heavily than the normal areas. They suggested that the penetration of dyes into the fibre was controlled by a thin surface layer relatively impermeable to large dye molecules. If this explanation is correct, one would anticipate a similar effect occurring with wool, since the surface of wool is covered by a thin hydrophobic layer, the epicuticle. Medley and Andrews [6] abraded the surface of wool fibres by rubbing them between ground-glass plates and showed that fibres so treated adsorbed dye more rapidly than unabraded fibres. Brown [7] has stated that mechanical damage to wool is usually characterised by fibrillation of the fibres, and the tendency of the cortical cells to separate with mechanical treatment is greatly accelerated by acid damage. This agrees with the observation of Parker [4] that carbonising before dyeing accentuates faults due to abrasion damage.

Townend [8], and Barritt and Elsworth [9] classified dyes according to their ability to cover mixtures of chlorinated and normal wool. More recent work [10] has shown that this classification is related to the hydrophobic–hydrophilic balance in the dye and the surface properties of the wool fibre. If, as has been suggested, abrasion of the wool fibre is characterised by fibrillation and scale removal, then it would be expected that those dyes recommended for covering carbonising faults on tippy-dyeing wool would also be the best for dealing with abrasion damage.

It has also been suggested that this type of fault is more prevalent at present than it was, e.g., 10 or 15 years ago and this has been ascribed to a lowering of the quality of the wool blends used in a given cloth. The statement has also been made that the inclusion of noil in a fabric increases the likelihood of the fault's occurring. This information, whilst throwing no light on the problem, is interesting in that it suggests that wool which is already physically or chemically damaged is more prone

to further damage than better-quality wools. As far as badly degraded wool is concerned, information has been elicited that shoddy pieces never show the fault. Presumably in this case the wool is originally so degraded and hydrophilic in character that further mechanical action cannot affect the surface characteristics of the fibre so far as dye absorption is concerned.

There is no doubt that this problem is a very serious one for the practical dyer, and it is the object of this paper to discuss the effect of abrasion of wool on the dyeing properties of wool dyes, to characterise the properties of individual wool dyes on abraded wool, and to obtain a practical method for avoiding the difficulties currently being encountered.

Experimental

PREPARATION OF ABRADED MATERIAL

The fabric used was a botany serge (6 oz, 2/2 twill, 60 picks/in., 70 ends/in.), and Grade 1 glass-paper (Naylor's, Woodley, Manchester) constituted the abradant. A standard Crockmeter (*BS* 2677: 1956) was used to obtain standard abrading conditions. A sample of serge (11 in. × 3 in.), with the length parallel to the warp yarns, was mounted under tension on the Crockmeter and a circle of glass-paper was fastened to the finger of the Crockmeter. The abradant was then moved to and fro 50 times over the material.

Samples of wool were abraded using (*a*) new glass-paper and (*b*) glass-paper that had already been used to abrade 24 samples of wool. The abraded wool was then dyed with 0·25% Lissamine Blue BFS (C.I. Acid Blue 18), using 3% sulphuric acid as dyebath assistant. Dyeings were commenced at 40°C and the dyebath was raised to the boil over 30 min. Samples were taken at this stage and also after boiling for 1 h. Examination of the dyeings showed that the differences in dye uptake between abraded and non-abraded areas of the cloth were not affected by the condition of the glass-paper. This test was repeated with 0·25% Naphthalene Scarlet 4RS (C.I. Acid Red 18) and 0·25% Tartrazine NS (C.I. Acid Yellow 23), and similar results were obtained. It was concluded that it was possible to obtain reproducible abrasion using the same sample of glass-paper for rubbing 25 samples of serge each 50 times.

It was also noticed that with the three dyes examined, the abraded area was dyed more heavily than the normal areas. In order to confirm that this effect was different from that encountered when abrasion followed dyeing, dyeings of 0·25% shades of Lissamine Fast Violet 2BS (C.I. Acid Violet 41), Solway Purple RS (C.I. Acid Violet 43), Solway Blue BNS (C.I. Acid Blue 45), Solway Blue RNS (C.I. Acid Blue 47), and Solway Blue 2GS (C.I. Acid Blue 40) were prepared by the usual method. After being dyed, the samples were dried and abraded in exactly the same manner as was the undyed serge. It was found that in all cases the abraded area appeared *lighter* than the unabraded areas. This effect is presumably an optical one arising from fibrillation of the fibres.

In subsequent investigations other methods of abrasion were used; these will be described later. However, unless it is stated otherwise, the method already described was used.

In addition to the use of worsted serge as standard material throughout the bulk of the experimental work, some tests were also carried out on a sample of a woollen velour cloth. Apart from slight differences in degree, presumably due to differences in cloth construction and wool quality, the effects on this material paralleled those obtained on the standard serge.

EFFECT OF ABRASION ON THE DYEING PROPERTIES OF LEVEL-DYEING ACID DYES

Effect of Time and Temperature

Samples of worsted serge were abraded and then dyed as follows.

Twelve identical dyebaths were prepared, each containing 0·25% dye and 3% sulphuric acid (168°Tw.), in a 50 : 1 liquor ratio. The abraded wool was wetted out for 2 min in boiling distilled water and cooled to 40°C. The samples were then introduced into the dyebaths at 40°C and the temperature raised at the rate of 2 deg. C/min. Dyeings were completed at the following temperatures and time intervals—

at 60, 80, and 90°C; after 10 min, 30 min, 1 h and 4 h at 90°C;
at 100°C; and after 10 min, 30 min, 1 h and 4 h at 100°C.

The dyeings were then rinsed and dried.

The temperature of 90°C was chosen to simulate the conditions obtaining in a normal open winch machine, and 100°C to simulate the effect of raising the effective temperature to the boil. The samples were examined visually for contrast in colour between the abraded and normal areas and assessments were made on the normal 1–5 scale (*BS* 2662:1956 Colour Fastness: Grey Scale for assessing Changes in Colour). The results are detailed in Table I.

The typical behaviour of a dye which shows good coverage of abraded wool and one which shows poor coverage is illustrated graphically in Fig. 1 and visually in Fig. 2. In Fig. 1, decreasing positive contrast from Grade 1 to Grade 5 is followed by the production of a negative contrast. It will be seen that the two dyes differ markedly in their behaviour. Propolan Yellow 3G (ICI) at 60°C gives a positive contrast of Grade 3, but when the temperature has reached 100°C, the abraded and normal areas are almost equal in depth and there is hardly any visible contrast (Grade 4–5). This state of affairs continues for a boiling time of 1 h, but when this is prolonged to 4 h a slight negative contrast (Grade 4–5) is seen, the abraded area being then visually lighter than the normal area. On the other hand, Naphthalene Red EAS (C.I. Acid Red 13) starts at 60°C to exhibit a strong positive contrast (Grade 2), which persists even after the temperature has been raised to the boil and boiling continued for 4 h, although the contrast is then much less marked (Grade 4–5). Thus, whereas Propolan Yellow 3G gives coverage of the fault after boiling for 1 h with, on further boiling, production of a slight negative effect, with Naphthalene Red EA, boiling for as long as 4 h will not

TABLE I

	Colour Index No. C.I. ACID	Maximum dyeing temperature† (°C)	60°C	80°C	90°C	Time and temperature of assessment: 100°C	10 min at final temperature	30 min at final temperature	1 h at final temperature	4 h at final temperature
Lissamine Fast Yellow 2G	Yellow 17	90	3	3–4	4		4–5	5	5	5
		100				4	4–5	5	5	5
Propolan Yellow 3G (ICI)		90	3	3–4	4		4–5	5	5	5
		100				4–5	5	5	5	4–5*
Tartrazine K	Yellow 27	90	3	3	4		4	5	5	5
		100				4	4–5	4–5	5	5
Tartrazine N	Yellow 23	90	2	3	3		3	3–4	4	4–5
		100				3	3	4	5	5
Lissamine Fast Yellow AE	Orange 3	90	3–4	4	4–5		5	5	5	5
		100				4–5	5	5	5	4*
Naphthalene Fast Orange 2G	Orange 10	90	3	3–4	3–4		3–4	4–5	5	5
		100				4	5	5	5	5
Naphthalene Scarlet R	Red 26	90	2	2	2		3	3	3–4	4
		100				3	3	3–4	4–5	5
Croceine Scarlet 3B	Red 73	90	2	2	2		2	2	3	3
		100				3	3	3	3–4	5
Naphthalene Red J	Red 88	90	3	3	3		3	3–4	4	4–5
		100				4	4–5	5	5	5
Naphthalene Red EA	Red 13	90	2	2	2		2	2	3	3
		100				2	2	3	3–4	5
Naphthalene Scarlet 4R	Red 18	90	2	2	2		2	2	2	3
		100				2	2	2	2	3–4
Azo Geranine 2G	Red 1	90	2	3	4		4	4–5	4–5	5
		100				4	4	5	5	5
Propolan Red 3G	Red 57	90	2	2	3		4	4	4–5	5
		100				4	5	5	5	4–5*
Lissamine Fast Red 4G	Red 30	90	2	2	2		3	3	3–4	4
		100				3	4	4–5	5	5
Carmoisine W	Red 14	90	2	2	2		2	2	2	3
		100				2	3	3–4	4	5
Solway Rubinol R	Red 80	90	2	2	3		3–4	4	4–5	5
		100				3	5	5	5	4–5*
Lissamine Red 6B	Violet 7	90	1	2	2		2	3	3–4	4–5
		100				2	3	4–5	5	5
Naphthalene Bordeaux B	Red 17	90	2	2	2		2	2	3	3–4
		100				3	3	3	3–4	5
Lissamine Red 7BP	Violet 5	90	1	1	1		2	2	2	3
		100				2	2	3	3	5
Lissamine Fast Red B	Red 37	90	2	2	2		2	3	3	3–4
		100				2	3	4	5	4–5*
Lissamine Fast Violet 2B	Violet 41	90	2	3	3–4		4	4–5	4–5	5
		100				4	5	5	5	5
Lissamine Violet 2R	Violet 1	90	1	1	1		1	2	2	3–4
		100				2	2	3–4	4–5	5
Lissamine Violet 10B	Blue 13	90	1	1	2		3	3–4	4–5	5
		100				3	4	4–5	5	4–5*
Solway Purple R	Violet 43	90	1	2	3		3	4	4	5
		100				3	5	4*	4*	3–4*
Lissamine Blue BF	Blue 18	90	1	1	1		2	2	3	3–4
		100				2	2	3	4	5
Solway Blue RN	Blue 47	90	1	2	3		3–4	4–5	4–5	5
		100				3	5	4–5*	4*	4*
Solway Blue BN	Blue 45	90	1	2	2		2	3	3	4
		100				3	4	5	5	5
Lissamine Ultra Blue AR	Blue 71	90	1	2	2		3	3–4	3–4	5
		100				4	5	5	4–5*	4–5*
Lissamine Ultra Sky R	Blue 67	90	2	3–4	4		4	4–5	5	5
		100				4–5	5	5	4–5*	4*
Solway Blue A	Blue 69	90	1	1	2		2	3	3–4	4
		100				2	3	5	5	5
Solway Blue 2G	Blue 40	90	2	3	4		4	4	4–5	5
		100				4–5	5	5	4–5*	4–5*
Solway Blue PFN (ICI)		90	1	2	2		2	3	3	4
		100				3	4	5	5	5
Disulphine Blue AN	Blue 7	90	1	2	2		2	3	3–4	4–5
		100				2	3	4–5	5	4–5
Disulphine Blue FFN	Blue 147	90	2	2	3–4		5	5	5	4*
		100				3–4	5	4–5*	4*	4*
Lissamine Green BN	Green 50	90	1	2	3		4	4–5	5	5
		100				3	4–5	5	5	5
Disulphine Green B	Green 9	90	1	1	2		3	4	4	4–5
		100				3	3–4	4–5	5	5
Naphthalene Green G	Green 3	90	1	1	2		3	4	4	4–5
		100				3	4	5	5	5
Lissamine Green V	Green 16	90	1	2	3		3–4	4–5	5	5
		100				3	4–5	5	5	5
Lissamine Navy FK (ICI)		90	1	2	2		3	3–4	4	4–5
		100				3	3–4	4	4–5	5
Lissamine Navy AN (ICI)		90	1	2	3		3	3–4	4	4–5
		100				3	3–4	4	4	4–5
Lissamine Navy Blue FG (ICI)		90	1	2	3		3–4	3–4	4	4–5
		100				3	3–4	3–4	4	5
Naphthalene Black 12B	Black 1	90	1	2	3		4	4	4	5
		100				3	4	4–5	4–5	5
Naphthalene Blue Black C	Black 41	90	1	2	3		4	4	4–5	5
		100				3	4	4–5	4–5	4–5

* Shows negative contrast, i.e. abraded areas less heavily dyed than normal ones.
† Normal assistants used.

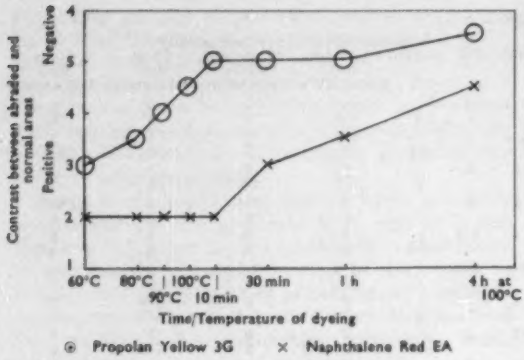

FIG. 1—Coverage of abrasion faults in dyeing

result in the production of a level dyeing, the abraded areas always being more heavily dyed than the normal areas.

Table I shows that the contrast between the abraded and unabraded areas is large in the early stages of dyeing, the amount of dye adsorbed by the abraded areas appearing to be greater than that adsorbed by the normal areas. As the time of dyeing increases, the contrast decreases until a level dyeing results, in most cases in less than 4 h. Levelness is achieved more rapidly at 100°C than at 90°C, as would be expected. With a number of dyes, prolonged boiling results in a further, but reversed, contrast being produced.

Some experiments were carried out to interpret these results quantitatively. Three dyeings were taken during the early stages of the dyeing operation when large positive contrasts were noted and three dyeings were also taken after boiling for 4 h where negative contrasts were obtained. The surface hairs were removed from the abraded and non-abraded areas with a scalpel. The amount removable from the abraded areas was approx. 10 mg. Equal weights of fibre from the abraded and unabraded areas were taken and the colour was removed by extraction with 10 ml of 25% aqueous pyridine. After filtering the solution through a sintered glass filter to remove the fibres, the dye content of the extracts was measured on a Unicam SP 600 spectrophotometer. The results obtained are given in Table II.

These results show conclusively that in the initial stages of dyeing the abraded areas of the fibre are in fact taking up more dye than the normal areas, and the visually observed effect is a real one. On the other hand, for those dyeings carried out for a long time at the boil, where visually slight negative effects were observed, the amounts of dye on the abraded and unabraded portions of the material are identical, and the observed effect is therefore an optical one due to fibrillation of the fibres in the abraded areas.

As far as practical dyeing is concerned, the results so far presented are of considerable importance. In a normal winch machine, although the liquor in the stuffing box may be boiling vigorously, the temperature of the liquor at the back of the machine will be only about 90°C. Thus, when the cooling effect of the cloth passing over the winch reel is also taken into account, the average cloth temperature is approx. 91–92°C and never approaches 100°C. The figures given in Table I show that at 90°C a very much longer time is required to achieve coverage of a standard abrasion fault than at 100°C. Thus, under normal winch-dyeing conditions the choice of dyes can also exert a profound influence on the ease of achieving covering of abrasion damage, and even at 90°C on prolonged dyeing it may be possible to obtain reversal of the contrast.

Effect of Dye Constitution

From the results given in Table I for dyeing at 100°C it is possible to classify dyes according to the time taken to cover the abrasion fault (see Table III). Because of the much lower rate of coverage at 90°C, classification at the lower temperature is more difficult.

This classification is reasonably well defined, and shows clearly the wide variation in the ability of level-dyeing acid dyes to cover abrasion damage at 100°C. From the practical point of view, two factors enter into play—(*a*) the relative initial strike of the dye on the abraded and normal areas of the material and (*b*) the ability of the dyes to migrate during boiling and thus level out the initial differences in strike. Consideration of Tables I and III suggests that migration is the more important of the two factors. This follows from the fact that, with all but six dyes, the contrast at 60°C between the abraded and unabraded areas is Grade 1 or 2, indicating a very big difference in initial adsorption of dye. Even when the temperature has reached 100°C, only ten dyes have reached a contrast of 4 or better, and of these six were those which at 60°C showed a lower contrast than 2 between the abraded and unabraded areas. In spite of this, about half the dyes examined gave level dyeings after boiling for only 30 min, showing how quickly levelness could be achieved when migration was possible.

The ability of a level-dyeing acid dye to cover chlorination damage or tippiness is related to its degree of sulphonation. There appears to be a similar close relation between sulphonation and

TABLE II

Dye	Time and temperature of dyeing	Dye on abraded wool / Dye on normal wool
Naphthalene Scarlet 4R	10 min at 90°C	1·60
Lissamine Violet 2R	10 min at 80°C	5·0
Disulphine Blue AN	10 min at 80°C	2·9
Propolan Red 3G	4 h at 100°C	1·01
Lissamine Ultra Blue AR	1 h at 100°C	0·99
Solway Blue RN	4 h at 100°C	1·00

TABLE III

Ability of Level-dyeing Acid Dyes to cover Abrasion Damage at 100°C

Group 1	Group 2	Group 3	Group 4	Group 5
Lissamine Fast Yellow AE	Lissamine Fast Yellow 2G	Lissamine Fast Red 4G	Tartrazine N	Naphthalene Red EA
Propolan Yellow 3G	Tartrazine K	Lissamine Fast Red B	Naphthalene Scarlet R	Croceine Scarlet 3B
Naphthalene Fast Orange 2G	Azo Geranine 2G	Lissamine Red 6B	Carmoisine W	Naphthalene Scarlet 4R
Propolan Red 3G	Naphthalene Red J	Lissamine Violet 10B	Naphthalene Bordeaux B	Lissamine Navy AN
Solway Rubinol R	Solway Blue BN	Disulphine Blue AN	Lissamine Red 7BP	Naphthalene Blue Black C
Solway Purple R	Solway Blue A	Disulphine Green B	Lissamine Violet 2R	
Lissamine Fast Violet 2B	Solway Blue PFN		Lissamine Blue BF	
Solway Blue RN	Lissamine Green BN		Lissamine Navy FK	
Lissamine Ultra Sky R	Naphthalene Green G		Lissamine Navy Blue FG	
Disulphine Blue FFN	Lissamine Green V		Naphthalene Black 12B	
Solway Blue 2G				
Lissamine Ultra Blue AR				

Group 1 level after 10 min at 100°C
Group 2 level after 30 min at 100°C
Group 3 level after 1 h at 100°C
Group 4 level after 4 h at 100°C
Group 5 NOT level even after 4 h at 100°C

ability to cover abrasion damage. Thus, all the dyes in Group 1 of Table III (with the exception of Naphthalene Fast Orange 2G) are monosulphonated. Group 2 contains only two monosulphonated dyes, the rest being dyes which are either disulphonated or are triphenylmethane (TPM) dyes. Group 3 contains no monosulphonated dyes, but a mixture of TPM dyes and disulphonated dyes. In Groups 4 and 5, all the dyes contain at least two sulphonate groups. This is illustrated graphically in Fig. 3.

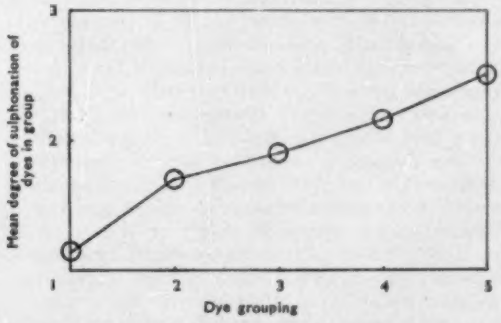

FIG. 3—Relation between degree of sulphonation of dye and ability to cover abrasion damage at 100°C

Monosulphonated dyes as a group are, therefore, better able to cover abrasion damage than the polysulphonated ones; in general, the classification in Table III agrees with that provided by Townend [11] for the coverage of mixtures of chlorinated and normal wool.

Compatibility in Mixture Dyeings

At this stage, discussions with piece dyers showed that the results obtained did not correspond with bulk experience with a number of important dyes. Since, under normal dyeing conditions, it is unusual to employ only one dye, it was thought that the apparent lack of agreement might result from the effect of dyeing with binary or ternary mixtures. To investigate this possibility, a fawn dyeing was made by means of yellow, red, and blue dyes. The yellow and red were chosen from Group 2 (Table III) and were unchanged throughout the experiment. The blue component was varied and included both mono- and di-sulphonated dyes from Groups 1 and 2. In addition, a lilac shade was produced by means of a violet dye and two different red dyes. Dyeing was carried out at 90°C by the method already described; the results are given in Table IV.

A very important effect is revealed by these results. In mixture dyeings the dye classification (and therefore the degree of sulphonation) determines the value of the recipe in covering abrasion faults. For example, with the three fawn shades which give on-tone dyeings (No. 5, 6 and 7) and lilac 2, which behaves similarly, the dyes used in the individual recipes are all of the same degree of sulphonation. Thus, in lilac 2, both dyes are monosulphonated, in fawns 5 and 6 they are disulphonated, and in fawn 7 the three dyes are monosulphonated. With the combinations that give off-tone dyeings, the dyes in the mixture are of different degrees of sulphonation.

Thus, to achieve a compatible combination, dyes should be chosen from the same group, which generally means they must have the same degree of sulphonation. The reason for this choice is the need to select dyes which have similar rates of strike on the abraded and unabraded areas, and similar rates of migration at the boil.

This observation is of the greatest importance for the formulation of dyeing recipes, and the apparent contradictions between bulk experience and the initial work described in this paper are resolved when it is borne in mind.

TABLE IV

Effect of Time and Temperature on Covering of Abrasion Damage in Mixture Dyeings

Shade	Recipe	Time and temperature of dyeing						
		60°C	80°C	90°C	10 min at 90°C	30 min at 90°C	1 h at 90°C	4 h at 90°C
Fawn 1	0·25% Lissamine Fast Yellow 2GS 0·14% Azo Geranine 2GS 0·065% Lissamine Ultra Blue ARS	1	1	2	2	2	3	3–4
		Abraded areas redder than unabraded						
Fawn 2	0·26% Lissamine Fast Yellow 2GS 0·12% Azo Geranine 2GS 0·048% Lissamine Fast Violet 2BS	1	1	2	2	2	3	3–4
		Abraded areas redder than unabraded						
Fawn 3	0·22% Lissamine Fast Yellow 2GS 0·15% Azo Geranine 2GS 0·075% Solway Blue 2GS	1	1	2	2	3	3	4
		Abraded areas redder than unabraded						
Fawn 4	0·25% Lissamine Fast Yellow 2GS 0·14% Azo Geranine 2GS 0·055% Lissamine Ultra Sky RS	1	1	2	2	2	3	3–4
		Abraded areas redder than unabraded						
Fawn 5	0·25% Lissamine Fast Yellow 2GS 0·14% Azo Geranine 2GS 0·046% Solway Blue PFN	1	1	2	3	3	4	4–5
		Abraded areas on tone with unabraded						
Fawn 6	0·27% Lissamine Fast Yellow 2GS 0·15% Azo Geranine 2GS 0·046% Solway Blue BN 150	1	1	2	2	3	3–4	4
		Abraded areas on tone with unabraded						
Fawn 7	0·49% Propolan Yellow 3GS 0·20% Propolan Red 3GS 0·09% Solway Blue 2GS	2	2	3	3–4	4	4–5	5
		Abraded areas on tone with unabraded						
Lilac 1	0·26% Lissamine Fast Violet 2BS 0·08% Azo Geranine 2GS	2	2	2	2	2	3–4	3–4
		Abraded areas redder than unabraded						
Lilac 2	0·26% Lissamine Fast Violet 2BS 0·10% Propolan Red 3GS	2	2	2	3	3–4	4	5
		Abraded areas on tone with unabraded						

Effect of Carbonising on Covering of Abrasion Damage

Carbonising of woollen pieces may be carried out either before or after dyeing, but the former is usually preferred since it obviates the possibility of change of colour of dyed pieces. It was decided to determine whether carbonising had any influence on the dyeing properties of abraded wool. To cover all possibilities, carbonising was carried out (*a*) on material that had already been abraded and (*b*) on normal material that was subsequently abraded.

The material was immersed for 15 min in a solution containing 50 g/l. of sulphuric acid (168°Tw. [66° Bé]) at a liquor ratio of 20:1. After impregnation the material was passed in open width between a pair of power-driven squeeze rollers giving an expression of 100%. After being dried in an oven at 70°C the material was baked at 105°C for 15 min.

Dyeing tests were then made as follows. The carbonised material was wetted out for 15 min at 40–45°C in water, at a liquor ratio of 30 : 1. The wetted-out material was then hydroextracted to 100% regain and dyed (at a 30 : 1 liquor ratio) with the addition of dye only to the dye liquor. This pretreatment gave an acid content of approximately 3% in the material and no further addition of acid was necessary for normal dyebath exhaustion. The acid content of all material pretreated by this method was uniform. The results obtained with a range of dyeings are given in Table V.

The relation between carbonising and abrasion is immediately seen to be important. If carbonising takes place before abrasion, subsequent dyeing gives a result which is slightly inferior in contrast to a dyeing on material which has only been abraded. On the other hand, if the material is abraded and subsequently carbonised, more rapid covering of the original abrasion fault results when the material is subsequently dyed. This behaviour is consistent throughout the series. It seems that where the material is carbonised first, uniform damage is caused. When the material is subsequently abraded, further local degradation is caused to the already damaged surface and this is reflected in the decreased ability of dyes to cover the fault. Where the material is originally abraded, however, subsequent overall damage during carbonising reduces the difference in the degree of damage between the abraded and non-abraded areas, and this is reflected in dyeing by the more rapid achievement of a uniform dyeing.

Relation with other Effects observed on Wool

One of the most important questions posed by the results already described is: "What is the effect of abrasion on the wool fibre surface?" Experiments have been carried out to provide an answer to this query and an explanation for the observed effects in dyeing.

The fact that, in the initial stages of dyeing, material that had been abraded adsorbed dye more rapidly than unabraded material suggested that the

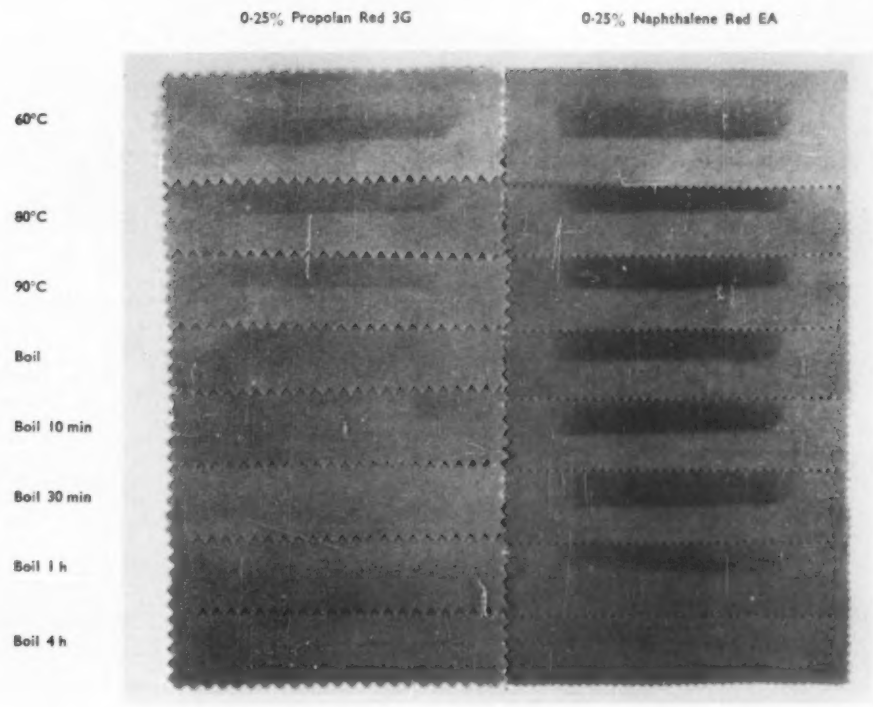

FIG. 2—Coverage of abrasion faults on dyeing

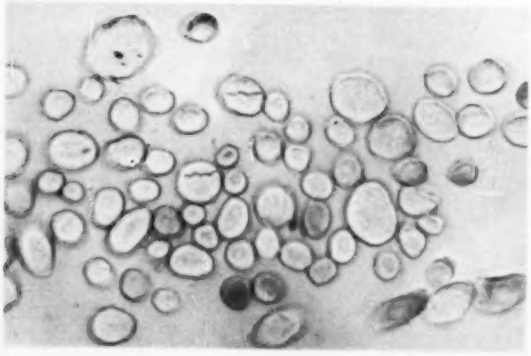

FIG. 4—Cross-section through normal portion of fabric (×225)

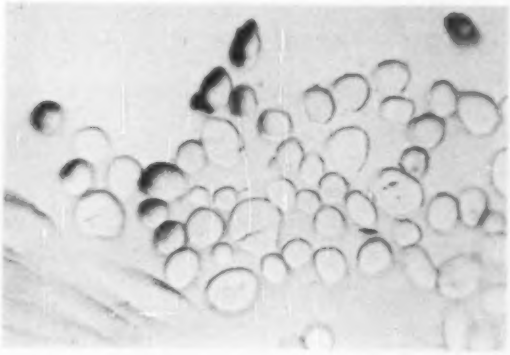

FIG. 5—Cross-section through abraded portion of fabric (×225)

FIG. 6— Deeply dyed, fibrillated fibres (× 750)

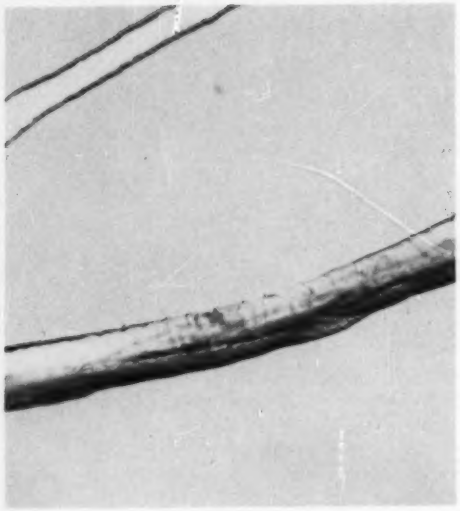

FIG. 7— Longitudinal sections of fibres from abraded areas after dyeing at 60°C (× 280)

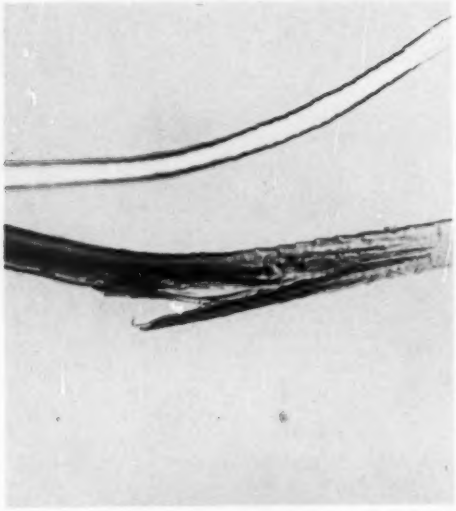

FIG. 8— Longitudinal sections of fibres from abraded areas after dyeing at 90°C (× 280)

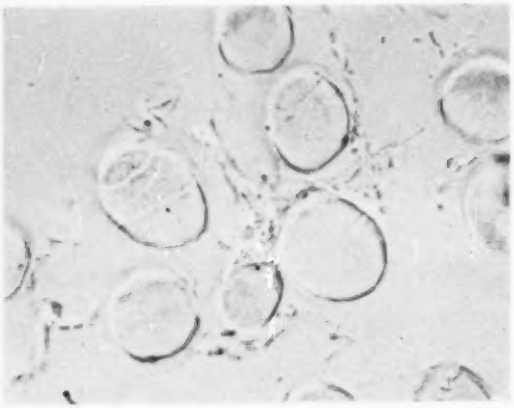

FIG. 9— Microphotograph of "anomalous" abraded fibre (× 600)

TABLE V

Effect of Carbonising on Covering of Abrasion Damage

Dye		Processing sequence	Contrast between abraded and unabraded areas						
			60°C	80°C	90°C	10 min at 90°C	30 min at 90°C	1 h at 90°C	4 h at 90°C
0·25%	Lissamine Fast Violet 2BS	Control (normal dyeing)	2	3	3–4	4	4–5	4–5	5
		Abrade then carbonise	2	3	4–5	4–5	5	5	5
		Carbonise then abrade	2	3	3–4	3–4	4	4–5	4–5
0·255%	Lissamine Fast Violet 2BS	Control (normal dyeing)	2R	2R	2R	2R	2R	3–4R	3–4R
0·08%	Azo Geranine 2GS	Abrade then carbonise	2R	2R	2R	3R	3–4R	4R	4–5R
		Carbonise then abrade	2R	2R	2R	2R	2R	3–4R	3–4R
0·25%	Lissamine Fast Yellow 2GS	Control (normal dyeing)	1	1	2	3	3	4	4–5
0·14%	Azo Geranine 2GS	Abrade then carbonise	2	3	3	3–4	3–4	4	4–5
0·046%	Solway Blue PFN	Carbonise then abrade	1	2	2	2	2	2	3–4
0·25%	Lissamine Fast Yellow 2GS	Control (normal dyeing)	1R	1R	2R	2R	2R	3R	3–4R
0·14%	Azo Geranine 2GS	Abrade then carbonise	2	2R	2R	3R	3R	3–4R	4R
0·065%	Lissamine Ultra Blue ARS	Carbonise then abrade	1R	1R	2R	2R	2R	2R	3–4R
0·27%	Lissamine Fast Yellow 2GS	] (normal dyeing)	1	1	2	2	3	3–4	4
0·15%	Azo Geranine 2GS	Abrade then carbonise	2	2	3	3	3–4	4	4–5
0·046%	Solway Blue BN 150	Carbonise then abrade	1	1	2	2	2	3	4
0·25%	Lissamine Fast Yellow 2GS	Control (normal dyeing)	1Y	1Y	2Y	2Y	3Y	3–4Y	4Y
0·07%	Coomassie Violet 2RS	Abrade then carbonise	3Y	3Y	3Y	3–4Y	4Y	4–5	5
		Carbonise then abrade	1Y	1Y	2Y	2Y	3Y	3Y	3–4Y

fibre had been made more hydrophilic. To measure this effect, the contact angles of normal and abraded wool fibres at an oil–water interface were measured by a method previously described [10]. The mean contact angles (average for 50 fibres) are— normal fibres $145 \pm 5°$, abraded fibres $105 \pm 5°$. The difference between the contact angles is significant and implies that abrasion makes the fibre surface more hydrophilic. The difference in contact angle is similar to that already reported [10] between the undyed and dyed areas of tippy-dyeing loose wool.

It was thought that this difference would also be observed in times of wetting. When the fabrics were spotted with water, although differences in wetting were apparent, the time taken to wet even the abraded areas was very long. The use of mixtures of water and ethyl alcohol was therefore investigated and was found to give more rapid wetting. Drops of known size of 30% ethyl alcohol in water were dropped on to normal and abraded wool and the times to wet out were measured. The abraded material was wetted out in 2 s, whereas the unabraded took 33 s to wet out.

It should be pointed out that whereas 30% ethyl alcohol in water was needed with the samples of dyed serge examined, with other materials the amount of alcohol may need to be varied owing to differences in physical characteristics. For example, at prolonged dyeing times, the proportion of alcohol had to be reduced in order to maintain approximately the same time of wetting of a sample of serge. This effect is probably caused by a gradual increase in the hydrophilic properties of the fibre surface with increased dyeing time.

Samples of cloth and the yarns and fibres from this material were examined microscopically. Fig. 4 and 5 show cross-sections through normal and abraded portions of the fabric. The latter shows the presence of heavily dyed, damaged fibres on the periphery of the yarn. No such damaged and heavily dyed fibres are visible in cross-sections of the normal fibre. Fig. 6 shows deeply dyed, fibrillated fibres on the yarn periphery with parts of the fibres broken away. Fig. 7 and 8 show longitudinal sections of fibres taken from abraded areas of the fibre after dyeing at 60 and 90°C. The extent of fibrillation and modification of the fibre surface are clearly visible. In Fig. 7, the scale structure on one side of the fibre is intact and shows little dyeing; the opposite surface, which is heavily dyed, shows an almost complete absence of scales. Fig. 8 is of an abraded fibre dyed at 90°C and shows the breaking away of portions of the fibre surface and penetration of dye into the fibrillated areas.

The evidence presented indicates that abrasion causes marked changes in the surface characteristics of the wool fibre. Scale removal and fibrillation are accompanied by increased ease of wettability of the fibre surface and a decrease in the contact angle at an oil–water interface. It is suggested that this effect is similar to that already reported for tippy-dyeing loose wool, and the results of dyeing experiments on abraded wool run parallel to those already reported on tippy-dyeing wool. It would be expected that the increased surface area available, combined with a more hydrophilic character, would result in increased adsorption of dye.

It is reasonable to expect, therefore, that the effect of adding cationic dyebath auxiliaries to dyebaths used for dyeing abraded wool would yield results similar to those observed with tippy-dyeing wool. In this case, addition of cationic agents caused a decrease in the differences in dye uptake between the tip (hydrophilic) and root (hydrophobic) portions of the fibre and resulted in the production of more uniform dyeings. Experiments were therefore undertaken to investigate the effect of this type of agent in the dyeing of abraded wool.

Effect of Dyebath Auxiliary Agents on Covering of Abrasion Damage

Lissolamine A 50% (cetyltrimethylammonium bromide) has been shown to be effective in minimising the differences in dyeing behaviour between the tips and roots of wool fibres. It was therefore selected as one of the agents for examination in connection with the covering of abrasion damage. An objection to the practical use of this agent is that with some acid dyes precipitation of a dye–agent complex of low solubility can occur. In order to overcome this, a non-ionic dispersing agent, e.g. Lubrol W, may be added to the dyebath. Dispersol CWL provides a typical example of a cationic auxiliary agent which does not yield an insoluble dye–agent complex.

Tests were carried out to determine the effect of (*a*) 3% Dispersol CWL, and (*b*) 1% Lissolamine A 50%, 1% Lubrol W in the covering of abrasion damage. The dyebath was set at 40°C with the requisite amounts of dye, 3% sulphuric acid (168°Tw.), and auxiliary agent. The abraded wool was introduced at 40°C, the temperature raised to 90°C over 25 min and held there for varying periods. Samples of dyed wool were removed at appropriate intervals and the contrast observed between the normal and abraded areas assessed as before. The results are given in Table VI.

The effect of the auxiliary product will be immediately obvious from these results. The achievement of solidity of dyeing between the abraded and unabraded areas of the material occurs much more rapidly in presence of the cationic dyebath auxiliaries. This effect is to be expected from the work already described on the surface properties of abraded wool.

As a result of these observations, a method is now available to the practical dyer to enable him to overcome the difficulties which he previously encountered when dyeing wool which had suffered abrasion damage.

Effect of Wool Quality on Abrasion Damage

During discussions with wool dyers on the subject of damage to wool during processing, one topic recurred constantly. This was the effect of wool blends on the frequency of unlevelness, no matter whether this could be attributed to carbonising, abrasion, or other factors. It was generally claimed that lowering of wool quality caused increased difficulty in dyeing. In view of the widespread concern expressed on this particular topic, it was decided to carry out a limited amount of work on this problem in connection with abrasion damage. There were available a number of samples of wool yarn, all spun to the same count, whose quality was known. The types of wool and the distribution of fibre diameters are given in Table VII.

TABLE VI

Effect of Cationic Dyebath Auxiliary Agents on Covering of Abrasion Damage

Dye	Auxiliaries	Contrast between abraded and unabraded wool						
		60°C	80°C	90°C	10 min at 90°C	30 min at 90°C	1 h at 90°C	4 h at 90°C
0·25% Propolan Red 3GS	None	2	2	3	4	4	4–5	5
	3% Dispersol CWL	3–4	4–5	5	5	5	5	5
	1% Lubrol W 1% Lissolamine A 50%	4	4–5	5	5	5	5	5
0·25% Naphthalene Red JS	None	3	3	3	3	3–4	4	4–5
	3% Dispersol CWL	4–5	4–5	5	5	5	5	5
	1% Lubrol W 1% Lissolamine A 50%	4–5	4–5	5	5	5	5	5
0·25% Naphthalene Red EAS	None	2	2	2	2	2	3	3
	3% Dispersol CWL	2	2	3–4	3–4	3–4	4	5
	1% Lubrol W 1% Lissolamine A 50%	2	3	3–4	3–4	4	4–5	5
0·25% Naphthalene Scarlet 4RS	None	2	2	2	2	2	2	3
	3% Dispersol CWL	2	2	3	3	3–4	4	4–5
	1% Lubrol W 1% Lissolamine A 50%	3	3	3–4	3–4	4	4–5	4–5
0·25% Azo Geranine 2GS	None	2	3	4	4	4–5	4–5	5
	3% Dispersol CWL	2	4	4–5	5	5	5	5
	1% Lubrol W 1% Lissolamine A 50%	3–4	4–5	5	5	5	5	5
0·26% Lissamine Fast Violet 2BS 0·08% Azo Geranine 2GS	None	2R	2R	2R	2R	2R	3–4R	3–4R
	3% Dispersol CWL	2R	3R	3R	3R	3R	3–4R	4R
0·26% Lissamine Fast Violet 2BS 0·10% Propolan Red 3GS	None	2	2	2	3	3–4	4	5
	3% Dispersol CWL	2	2	3	3–4	4–5	5	5
0·25% Lissamine Ultra Sky RS 0·13% Coomassie Violet 2RS	None	1	2	2	3	3	4	4
	3% Dispersol CWL	2R	3R	3–4R	4R	4–5	5	5

TABLE VII

Range of Fibre Diameters in Different Yarn Samples (spun to 2/16s count)

Sample No.	Wool type and preparation	Percentage of fibres of diameter (μ)						Mean fibre diameter (μ)
		< 20	20–29	30–39	40–49	50–59	> 59	
1	52s prepared N.Z.	0·4	6·9	24·9	35·1	23·2	11·5	44·2
2	58s carded Australian	0·8	11·6	31·0	35·4	16·0	5·2	40·8
3	46s carded BA	0·6	19·6	44·6	26·3	7·6	1·3	36·1
4	54s prepared English	0·4	16·4	40·2	29·4	12·4	1·4	36·3
5	56s prepared N.Z.	2·8	35·6	33·1	19·3	7·4	1·8	33·2
6	48s prepared English	4	28·5	38·25	22·75	5·75	0·75	34·1
7	50s prepared N.Z.	1·2	28·2	46·8	17·6	5·8	0·4	33·6
8	64s prepared Australian	8	56·6	32·2	3·0	0·2	—	26·6

These samples have been arranged roughly in order of mean fibre diameter and range from 44·2 to 26·6 μ in mean diameter and include both woollen- and worsted-spun yarns. The nominal quality covers a very wide range from 46s to 64s so that there are, as will be seen from Table VII, large variations in the distribution of fibre diameters in the different samples.

Because of the limited amounts of yarn available it was not possible to prepare woven cloths, but knitted panels incorporating a rib structure, to impart as much dimensional stability as possible to the fabric, were prepared under controlled conditions. Samples of the knitted fabric were abraded and subsequently dyed under a variety of conditions with two- and three-colour combinations. Samples of each of the eight fabrics were dyed together in the same dyebath. The results obtained are detailed in Table VIII.

Here again the significant effect of Dispersol CWL in improving the covering of abrasion damage is seen, and a general pattern seems to emerge. Samples 3 and 6 tend to show less contrast between abraded and unabraded areas than the rest of the samples, and samples 1 and 8 greater contrast and less sensitivity to time of dyeing than the remainder. Samples 3 and 6 are of 46s and 48s quality, whereas samples 1 and 8 are of 50s and 64s quality, respectively. There is, therefore, no evidence of any direct relation between mean fibre diameter and the sensitivity of the fibre to abrasion damage or the ease of covering of this type of damage.

Relation of Artificial Laboratory Abrasion Damage to Practical Problems

In all the tests so far described, abrasion has been carried out in a standard manner using No. 1 glass-paper as the abrading medium. This was used to obtain a standard rub which was reproducible and is obviously divorced from the conditions likely to be encountered in practice. Under practical conditions, abrasion of piece goods is most likely to be caused in (*a*) milling machines, (*b*) dolly-scouring machines, and (*c*) winch-dyeing machines. Abrasion would normally occur wet under either acid or alkaline conditions and would be caused by either (*a*) wool-to-wool friction, or (*b*) wool-to-machine surface friction.

Experiments were therefore designed to determine whether wool–wool rubbing under wet acid or alkaline conditions would give effects similar to those obtained by rubbing with dry glass-paper. Samples of wool serge were abraded by the methods—

(1) Normal, dry, 50 rubs with No. 1 glass-paper

(2) Serge wetted out in boiling water, abraded with grade 150 wet-or-dry paper (Minnesota Mining and Mfg. Co. Ltd.)— 25 rubs

(3) Serge wetted out in boiling water and abraded with serge— 200 rubs

(4) Serge wetted out by boiling for 15 min with 3% sulphuric acid, 10% Glaubers salt, abraded wet with serge— 200 rubs

TABLE VIII

Effect of Wool Quality on Covering of Abrasion Damage

Dye recipe	Dyeing conditions	Contrast between abraded and non-abraded areas — Wool sample							
		1	2	3	4	5	6	7	8
0·26% Lissamine Fast Yellow 2GS	3% Sulphuric acid, 10 min at 90°C	2R	1R	3R	3R	3R	3R	2R	2R
	3% Sulphuric acid, 1 h at 90°C	2R	3R	3–4R	3R	3R	3–4R	2R	2R
0·12% Azo Geranine 2GS 0·048% Lissamine Fast Violet 2BS	3% Sulphuric acid + 3% Dispersol CWL, 10 min at 90°C	2R	3–4R	4R	3–4R	3–4R	4R	3R	3R
	3% Sulphuric acid + 3% Dispersol CWL, 1 h at 90°C	4R	4–5R	5	4R	4–5R	4–5R	4–5R	4R
0·25% Lissamine Fast Yellow 2GS	3% Sulphuric acid, 10 min at 90°C	2R	2R	3R	2R	2R	2R	2R	2R
	3% Sulphuric acid, 1 h at 90°C	2R	3R	4R	3R	4R	4R	3R	2R
0·14% Azo Geranine 2GS 0·046% Solway Blue PFN	3% Sulphuric acid + 3% Dispersol CWL, 10 min at 90°C	3	4	4–5	4	4–5	4–5	4	3–4
	3% Sulphuric acid + 3% Dispersol CWL, 1 h at 90°C	3–4	5	4–5	4–5	4–5	4–5	4–5	4

TABLE IX

Effect of Different Abrasion Treatments on Dyeing with 0·25% Lissamine Ultra Blue ARS

Abrasion method (details in text)	Contrast between abraded and unabraded wool						
	60°C	80°C	90°C	10 min at 90°C	30 min at 90°C	1 h at 90°C	4 h at 90°C
Method 1	1	2	2	3	3–4	3–4	5
Method 2	1	2	2	3	3–4	3–4	4–5
Method 3	1	2	2	3	4	4–5	5
Method 4	1	2	2	3	4	4–5	5
Method 5	1	2	3	4	4	4–5	5

(5) Serge wetted out for 15 min at 50°C with 5 g/l. soap flakes, 2 g/l. soda ash, abraded wet with serge— 200 rubs.

Samples of material abraded by these five methods were then dyed with 0·25% Propolan Red 3GS and 3% sulphuric acid, dyeing being started at 40°C, the temperature raised to 90°C and held there for 10 min. In all cases a Grade 4 contrast was obtained, indicating that similar degrees of abrasion were being obtained by each of the abrasive methods.

Dyeings were therefore prepared using 0·25% Lissamine Ultra Blue ARS, samples being taken at 60, 80, and 90°C, and at various times of dyeing at 90°C up to 4 h to see whether, over the whole dyeing operation, similar effects were obtained. The results are given in Table IX.

Thus, so far as abrasion of wool with wool is concerned, acid, alkaline, and neutral conditions all produce similar effects on dyeing properties. It is clear that serious effects can be obtained under all these pH conditions and could give rise to difficulties in dyeing. Microscopical examination of the surface fibres showed no differences in characteristics between the samples abraded with wool. Whilst the achievement of solidity of shade takes the same time as with wool abraded dry with glass-paper, after boiling for 30 or 60 min the material abraded with wool gives slightly improved coverage compared with that abraded with glass-paper. Wool abraded wet with grade 150 wet-or-dry paper behaved similarly to that abraded dry with glass-paper. It is concluded therefore that the result obtained should give a basis for bulk working where wool has been abraded by contact with other wool material.

In all the work so far described, "positive" effects (i.e. abraded areas are dyed more heavily than the unabraded) have always been obtained, except in a very small number of cases when prolonged dyeing times have been used. It has recently been reported [12] that when fabrics are rubbed against corroded or pitted stainless steel, scuff or abrasion marks may be formed. It is stated that these marks appear lighter in depth as though less dye had been adsorbed, and that "shedding" of the fibre surface has caused the fibre to reflect more light and the dyeing to appear weaker. This agrees with our observation on the abrasion of dyed wool, where the abraded area appeared weaker than the unabraded areas. There is, however, no information on the effect of rubbing against pitted stainless steel on the dyeing properties of the rubbed material.

This is a subject which has been omitted from the present work, but in one particular case of abrasion a "negative" contrast was produced. When a sample of wetted-out serge was abraded with Grade 320 wet-or-dry paper and subsequently dyed with 0·25% Lissamine Ultra Blue ARS, the abraded area was found to dye more weakly (Grade 2) than the unabraded area. This persisted even after dyeing for 1 h at 90°C, and when the dyeing was prolonged to 4 h at 90°C, levelness was still not achieved, the abraded area still being slightly weaker (Grade 4–5) than the unabraded area. This result was so completely different from all those previously obtained that the abrasion and dyeings were repeated; identical results were obtained. Microscopical examination of these abraded fibres showed that the effect was different from that found previously. Small particles of some substance appeared to surround many of the fibres and the absence of dyeing appeared to be associated with this phenomenon. This effect is shown in Fig. 9, which is a photomicrograph of this type of abraded fibre.

Conclusions

From the work described the following conclusions may be drawn—

Abrasion of wool, either wet or dry, can result in difficulties in dyeing. When abrasion takes place before dyeing, a positive contrast usually results, i.e. the abraded areas dye initially more heavily than the unabraded areas. The longer the dyeing time and the higher the dyeing temperature, the easier will be the covering of the initial fault. In some cases, after prolonged dyeing at 100°C a positive contrast may reverse and the abrasion is seen as a light area, i.e., a negative contrast. When abrasion takes place after dyeing, negative contrast results, owing to an optical effect caused by fibrillation of the fibres.

Rubbing of wool against wool produces an effect identical with that obtained on production of abrasion faults by artificial means, using glass-paper or other abrasives. Thus, in addition to any trouble encountered in practice due to the rubbing of wool against rollers in dolly scourers or milling machines, the contact of pieces with one another in this type of machine or even in ordinary winch-dyeing machines may also give rise to dyeing difficulties.

The time of dyeing required to achieve solidity of shade on abraded wool varies widely from dye to dye, and the most important factor of dye constitution affecting the ease of covering of abraded wool is the degree of sulphonation of the dye. It is

suggested that, in order to achieve the most successful practical dyeing results, when mixture dyeings are being made, dyes of similar degrees of sulphonation should be used. Monosulphonated dyes are, in general, more satisfactory than polysulphonated dyes.

Addition of certain cationic dyebath auxiliary agents has a significant effect in increasing the rate at which solidity of shade is achieved on abraded wool with all acid dyes. Dispersol CWL is particularly effective for this purpose.

The effect of abrasion is to cause fibrillation of the fibre and to increase the hydrophilic nature of the fibre surface. This effect is similar to that encountered in tippy-dyeing loose wool

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References

[1] Townend, J.S.D.C., **60**, 144 (1944).
[2] O'Day, *Amer. Dyestuff Rep.*, **34**, 157 (1945).
[3] Townend and Simpson, J.S.D.C., **62**, 47 (1946).
[4] Parker, *ibid.*, **74**, 693 (1958).
[5] Jenkins and Keels, *Amer. Dyestuff Rep.*, **39**, P660 (1950).
[6] Medley and Andrews, *Text. Research J.*, **29**, 398 (1959).
[7] Brown, J.S.D.C., **75**, 11 (1959).
[8] Townend, *ibid.*, **61**, 144 (1945).
[9] Barritt and Elsworth, *ibid.*, **64**, 19 (1948).
[10] Hadfield and Lemin, *ibid.*, **77**, 97 (1961).
[11] Townend, *ibid.*, **61**, 144 (1945).
[12] *Dyer*, **125**, 664 (1961).

Discussion

Mr. D. MARTIN: Have the lecturers examined the possibility of using coacervation methods in this field and, if so, what results have they obtained?

Mr. LEMIN: We have not carried out any experimental work on the possible use of coacervation methods for the covering of abrasion or similar types of wool damage. Theoretically, there would appear to be no reason why such methods should not work, since the agent-rich phase will be more hydrophobic than the water-rich phase. Provided that the dye or dye–agent complex will pass into the agent-rich phase, this will result in the dye being able to give improved coverage of wool damage.

Dr. G. H. LISTER: The position would appear to be that the abraded portion of the material is more accessible to dye at low temperatures and is therefore initially dyed darker; the subsequent events will be controlled by the efficiency of the migrating system. As the lecturers have carried out most of their work on level-dyeing acid dyes, for which the most efficient migrating system is that using Glauber's salt, was there any special reason why tests using this levelling agent were not included in the work?

Is any evidence available that cationic compounds of the type of Dispersol CWL will, in fact, complex with dyes of the type of Xylene Light Yellow 2G?

In my experience abrasion faults in practical dyeing occur in two fields: (1) carbonised wool pieces, where the abrasion resistance has been reduced by carbonising and the efficiency of migration is so great with level-dyeing acid dyes plus Glauber's salt that the practical fault formed is nearly always a "negative" one, and (2) with tightly twisted yarn in worsted pieces, where the use of faster dyes leads to a "positive" fault. Would the lecturers not agree, however, that the attainment of apparent solidity between abraded and normal portions of the wool is purely a matter of chance. When the migrating system is designed to give maximum efficiency, will this not always produce a "negative" fault?

Mr. HADFIELD: We would agree with Dr. Lister that the abraded areas of the material are more accessible to dyes at the start of dyeing and this will result initially in a strongly positive fault. We also agree that once this state of affairs has been achieved, the production of a final level dyeing will be mainly dependent on the migration properties of the system. A consideration of the results given in Table I indicates that with many dyes at 90°C (the normal temperature achieved in an open winch) levelness is not achieved even after four hours' dyeing. The reason, therefore, for using Dispersol CWL was to achieve an initially more uniform adsorption of dye so that the need for good migration was diminished. It is agreed that the addition of Glauber's salt would reduce the time required to eliminate positive abrasion faults, but in our opinion it is still preferable to reduce the initial fault to a minimum by using a complexing agent. We have obtained direct evidence (based on partition experiments) that even strongly hydrophilic dyes, e.g. Lissamine Fast Yellow 2GS or Naphthalene Scarlet 4RS, form complexes with Dispersol CWL under acid conditions at low temperatures.

Mr. A. J. HALL: A long time ago I dyed individual wool fibres held under tension and surprisingly found that, unlike viscose rayon fibres dyed similarly, the wool fibres were more deeply dyed than when dyed without tension. This behaviour was attributed to the effect of disturbing or loosening the outer membranes of the wool fibres, thus diminishing their normal resistance to dye penetration. Abrasion apparently acts in a way similar to stretching in disturbing the fibre structure, and it would be interesting to know if individual abraded wool fibres dyed under tension

behave similarly to non-abraded fibres, as indicated above.

Mr. HADFIELD: We wish to thank Mr. Hall for his comments. We would agree with the explanation advanced to explain the deeper dyeing of loose wool fibres dyed under tension.

Mr. R. J. HANNAY: Are the effects described in this paper due solely to the action of abrasion on the wool itself or has the presence of residual oil or fat from the original wool or from the previous scouring operation any influence on the results obtained? In other words, would the same effects be noticed with wool that had been completely solvent-extracted before abrasion and dyeing?

Mr. LEMIN: The effects described in the paper are the consequence of the action of abrasion on the surface of the fibre, i.e. the fibre becomes more hydrophilic in character and therefore more accessible to normal wool dyes. It would not be expected that different results would be obtained on fibres completely free from residual oil or grease and this has been confirmed with fully scoured and extracted material.

Mr. D. SIMS: How far do surface effects, e.g. root to tip variations, influence the dyeing of wool hanks at the boil with the faster types of dye?

Mr. HADFIELD: The present work on abrasion has shown that the effect is similar to that observed on "tippy" wool. The use of hydrophobic dyes, i.e. those of low sulphonation, is to be preferred when dyeing wool that has been abraded or is tippy and, in general, the milling acid dyes tend to be more hydrophobic than level-dyeing acid dyes. Apart, therefore, from any question of the inferior migration properties of milling acid dyes, they do tend in the initial stages of dyeing to show smaller differences in adsorption on different portions of the fibre than do level-dyeing acid dyes. Again, the use of cationic products, e.g. Dispersol CWL, gives improved results with milling acid dyes.

Dr. Ir. H. C. A. van Beek: The lecturers mentioned measurements of contact angles at an oil–water interface of normal and abraded wool fibres, as well as the wetting time with 30% ethyl alcohol.

The easier wettability of the damaged fibres seems to be an explanation for the fact that damaged parts of the fibres dye more quickly than the undamaged parts. The question then arises whether the addition of cationic agents to the dye-bath affects the wetting properties of the fibres. If such an addition reduces the difference in the wetting properties of damaged and undamaged fibres, this could also be an explanation for the levelling properties of cationic agents. Did the lecturers actually measure the wettability of normal and abraded wool fibres in presence of the cationic agents used?

Mr. LEMIN: We have measured the ease of wetting of the normal and abraded portions of wool dyed in the presence of cationic agents and find that the results parallel those given in the paper. It is suggested that the cationic agent does not affect differentially the wetting properties of the fibre, but rather is affecting the dyeing properties of the dyes, enabling more dye to be adsorbed by the normal areas of the material in presence of the agent than in its absence.

Effect of Dyeing and Related Processes on some Physical Characteristics of Wool

J. ELLIOTT, N. OLDFIELD, C. B. STEVENS, and C. S. WHEWELL

Values are given for the percentage reduction in the work to stretch wool fibres (% RW) after various treatments similar to those likely to be encountered in preparation and dyeing. Special attention is given to the changes brought about by solvent-assisted dyeing processes. In mild acid and alkaline treatments, low values are obtained if the temperature does not exceed 70°C, but above this temperature the % RW increases rapidly. Although under the conditions recommended for solvent-assisted dyeing the % RW is small, the presence of solvent increases the % RW if fibres are treated for long times at high temperatures. This suggests that under these conditions irreversible changes are brought about by the solvent. Measurements of breaking load and extension of yarns treated under various conditions show that greater degradation is produced when yarns are treated first in an acid solution and then in alkali than when the treatments are in the reverse order. This phenomenon was not observed in successive dyeing and sodium carbonate treatments. In these cases the total reduction in yarn tensile strength was considerably less than the sum of the reductions brought about by individual treatments, except where dyeing was carried out at pH 2.

Introduction

During processing, wool is subjected to a variety of wet treatments, including scouring, milling, carbonising, and dyeing. Scouring is carried out under alkaline conditions; milling under alkaline and sometimes acid conditions; carbonising under acid conditions; and dyeing under conditions which range from neutral or even very slightly alkaline to strongly acid. It has long been realised that during such treatments changes occur in the fibre, and the nature and extent of these changes have been studied by several workers [1].

Preliminary work in these laboratories had, however, suggested that the effect of successive treatments in acid and alkaline solutions depends upon the order of such treatments when they are different in character. It was therefore decided to determine quantitatively the effect of treating wool in solutions of sulphuric acid ranging in normality from 0·01 to 0·1 N and in buffer solutions of pH within the range 7–9·15. This was followed by an examination of the changes brought about by solutions similar to those used in commercial scouring and dyeing.

In addition, the introduction of solvent-assisted dyeing processes based on the addition to the dyebath of such solvents as benzyl alcohol prompted the study of the effect of these additions on the properties of the fibre. Evidence was already available to show that reduction in time or temperature of dyeing, or in both, results in less adverse change taking place, and consequently the claim that time and temperature of dyeing can be reduced by adding solvents to the dyebath becomes more important because at the same time the desirable characteristics of the fibre are preserved. Quantitative information on the magnitude of the changes taking place is, however, not available and it was to rectify this situation that the present investigation was undertaken.

Of the many ways suggested for estimating the degree of modification occurring in wool during processing, those based on measurement of physical properties, particularly breaking load and elongation of fibres, yarns, and cloths under standard conditions of temperature, relative humidity, and rate of loading are widely used because they are direct and sensitive. The behaviour of a single fibre is much less complicated than that of an assembly of fibres and determination of the load–extension characteristics of single fibres often yields information of more fundamental significance. Measurements of the tensile strength and extensibility of yarns and cloth, are, however, often favoured in practice as they give useful information on properties which are often closely related to performance of the material. At the same time, they are comparatively easy to carry out, unlike measurements on single fibres, which require delicate apparatus and are time-consuming.

Experimental

(*a*) *Loose wool: Single fibres* These were obtained from a Lincoln fleece. The root ends only were used.

(*b*) *Yarn* 3/12s Worsted wool yarn with 3·4 turns/in. twist was used.

(*c*) *Wool serge*, scoured and prepared for dyeing, was used as bulking material in the experiments on single fibres.

Before use, all the materials were Soxhlet-extracted, first with ether for 24 h and then with ethyl alcohol (64 O.P.) for 24 h, and then washed in running tap water for 18 h and in repeated changes of distilled water. Finally, they were conditioned at 22·2°C and 65% r.h.

(*d*) *Buffer solutions* The buffer solutions used were as follows—

pH	*Composition*
6·98	Disodium hydrogen phosphate (60 ml M/15 soln.) + potassium dihydrogen phosphate (40 ml M/15 soln.)
8·04	Disodium hydrogen phosphate (95 ml M/15 soln.) + potassium dihydrogen phosphate (5 ml M/15 soln.)
9·15	Sodium borate (M/20 soln.)

These will subsequently be referred to as pH 7, pH 8, and pH 9·15 buffer solutions, respectively.

(*e*) *Dyes* Commercial qualities were used.

(*f*) *Solvents* n-Butyl alcohol and benzyl alcohol were of analytical reagent quality.

Methods

DETERMINATION OF LOAD–EXTENSION CHARACTERISTICS

Yarn

The breaking loads of yarn were determined at 22·2°C and 65% r.h. by means of a Baer Yarn Tester, using both wet and dry samples. Test lengths of 12 in. and 1 mm were used, the former because it is the conventional test length and the latter because by using this very short length of yarn the significance of complicating frictional effects is reduced.

Single Fibres

Fibres, suitably mounted, were stretched to 30% extension under constant rate of loading on a Cambridge Fibre Extensometer and then allowed to contract to their original length, the load being removed at the same rate at which it was applied. This was done before and after a particular treatment or series of treatments and the area contained by the load–extension curve of the treated fibre was compared with that of the curve of the original "calibrated" fibre. The percentage reduction in work required to stretch the fibre (% RW) was regarded a measure of the extent to which the treated fibre had been modified. The fibres used for this work were selected by microscopic examination, medullated fibres and fibres of irregular diameter being rejected.

The effect of a particular treatment on the load–extension characteristics of single fibres was determined as follows. In each experiment not less than six calibrated fibres were used. Each set of fibres was attached to wool serge bulking material, which in turn was fastened to glass frames fitted to the vertically moving arms of a Marney dyeing machine. The whole assembly was agitated in the particular solution contained in glass vessels supported in the thermostatically controlled water bath of the machine. In those experiments where the temperature of treatment was 80–100°C, the vessels were fitted with reflux condensers. For treatments at 105°C the assembly was placed in the appropriate solution in a stainless steel jar of the standard type used in the Wash Wheel. The lid of the jar was then secured and the pot placed in the pressure vessel of a laboratory-scale dyeing machine. The temperature inside the vessel was raised to 105°C as quickly as possible (approx. 6 min) and maintained there for the required time. The pressure was then released, the pot cooled rapidly in running water, and the fibres removed for washing before their load–extension characteristics were determined. In all cases the treated fibres were washed in running water for 3 h and in several changes of distilled water for 12 h. The solution : material ratio was 100 : 1.

Treatments of yarn were carried out as follows. Hanks (3·0 g conditioned weight) were treated in the appropriate solution at the boil under reflux in 500-ml conical flasks at a solution : material ratio of 100 : 1. After the treatment, the samples were washed in running water for 3 h and then in several changes of distilled water during the next 12 h before being dried and conditioned at 22·2°C and 65% r.h. When the samples were subjected to a second treatment, the intermediate washing was for 1 h in running water and then in several changes of distilled water during the next hour. In the experiments carried out at 105°C a Franke high-temperature dyeing machine was used in which the samples were agitated mechanically throughout the treatment. Treatment was commenced cold, the temperature raised to 105°C in 15 min and treatment continued at 105°C for the required time. The washing procedure was the same as for the treatments at 100°C. Treatments at 60°C were carried out in a Marney dyeing machine. The samples, supported on frames, were agitated in appropriate solutions contained in glass vessels supported in the water bath of the machine. The washing procedure was the same as in the other experiments.

Results and Discussion

THE EFFECT OF TREATMENTS OF SINGLE FIBRES

Treatment in Acid and Alkaline Solutions

Calibrated wool fibres in sets of six were treated in solutions of sulphuric acid of concentration

TABLE I

Effect of Treatment of Single Fibres in Acid and Alkaline Solutions

Treatment in Buffer	Treatment in H_2SO_4	Temp. (°C)	Time (h)	Mean reduction in work (% RW)	
pH 8		40	1	2·7	(4)*
pH 8			2	3·9	(6)
	0·05 N		1	0·2	(4)
	0·1 N		1	3·1	(5)
	0·1 N		2	6·6	(4)
pH 8		60	1	3·5	(5)
pH 8			2	5·7	(5)
pH 9·15			1	3·0	(4)
pH 9·15			2	4·7	(5)
	0·02 N		1	1·5	(5)
	0·02 N		2	3·2	(6)
	0·05 N		1	2·2	(4)
	0·05 N		2	3·9	(5)
	0·1 N		1	2·4	(5)
	0·1 N		2	4·7	(5)
pH 8		70	1	5·2	(12)†
pH 8			2	6·0	(4)
pH 9·15			1	5·1	(4)
	0·05 N		2	5·5	(17)†
	0·01 N		2	6·0	(4)
pH 9·15		80	1	14·8	(1)‡
	0·1 N		2	11·7	(9)‡
pH 7		100	1	9·1	(4)
pH 8			1	18·5	(5)
pH 9·15			1	—	(0)
	0·01 N		2	15·4	(6)
	0·02 N		2	18·9	(6)
	0·1 N		2	25·6	(4)

* The figure in parentheses indicates the number of fibres (out of a total of 6) which remained intact throughout the experiments.

† 18 Fibres were used in these tests.

‡ 9 Fibres were used in these tests.

TABLE II

Effect of Treatment of Single Fibres in n-Butyl Alcohol

Conditions	Temp. (°C)	% Reduction in work after treatment for 1 h	4 h	8 h	16 h
Water	60	3·81	4·32	4·71	5·38
	100	10·78	14·38	14·83	18·36
8% (v/v) butyl alcohol	60	4·92	5·23	5·58	5·63
	100	14·66	16·85	23·90	32·72
8% (v/v) butyl alcohol + 1% Irgacet Scarlet RL	60	3·41	3·73	4·00	3·84
	100	10·05	16·37	20·06	31·62
8% (v/v) butyl alcohol + 8% Irgacet Scarlet RL	60	2·40	3·64	4·11	4·66
	100	8·41	10·82	17·61	26·18
8% (v/v) butyl alcohol + 1% Irgalan Brown Violet DL	60	3·05	4·16	4·42	5·76
	100	12·50	15·75	18·96	28·64
8% (v/v) butyl alcohol + 8% Irgalan Brown Violet DL	60	3·59	4·00	3·62	4·67
	100	10·43	12·60	15·52	26·46

0·01–0·1 N and in buffer solutions of pH 7, 8, and 9·15 for up to 2 h at 40, 60, 70, 80, and 100°C, respectively. The results of these treatments are listed in Table I.

The interesting feature of the results is the relatively low reduction in work obtained at temperatures not exceeding 70°C. Above this temperature the percentage reduction in work increased rapidly, particularly under alkaline conditions, so that at 80°C a value of 14·8% was obtained. Eight out of nine fibres treated at pH 9·15 broke before 30% extension was reached, and all six broke at 100°C.

Treatment in Solutions of Solvents

Two solvents were used— n-butyl alcohol and benzyl alcohol. Both have been used extensively in quantitative studies of the mechanism of solvent-assisted dyeing of wool [2]. n-Butyl alcohol was the first organic solvent observed to produce a marked increase in the rate of uptake of dyes by wool, particularly at low temperatures [3], while benzyl alcohol has been recommended as a suitable solvent for use in dyeing loose wool, slubbing, and yarn [4].

n-Butyl Alcohol

Selected fibres (six per experiment) were calibrated by stretching to 30% extension in distilled water at 22·2°C and then treated in an 8% (v/v) solution of n-butyl alcohol at 60°C or at 100°C for times ranging from 1 to 16 h. They were then stretched. Parallel series of experiments were carried out in presence of two 2 : 1 metal–dye complexes, Irgacet Brown Violet DL (Gy) and Irgacet Scarlet RL (Gy). The percentage reduction in work obtained is given in Table II.

It will be seen that the maximum reduction in work to stretch at 60°C was less than 6%, even after treatment for 16 h, and was very little greater than that produced by treatment in water. At 100°C, treatment for 1 h in presence of solvent increased the % RW to 14·6%, compared with 10·8% in presence of water alone, while after treatment for 16 h the corresponding figures were 32·7% and 18·4%. This important observation will be discussed later, together with the values for the reduction in work caused by boiling fibres in aqueous benzyl alcohol.

TABLE III

Effect of Treatment of Single Fibres in Water and in Benzyl Alcohol

Temp. (°C)	Time (h)	% Reduction in work to stretch in Water	3% Benzyl alcohol	3% Benzyl alcohol + 2% Irgalan Grey BL	3% Benzyl alcohol + 8% Irgalan Grey BL
60	2	2·51	3·43	4·05	3·34
	4	3·53	4·25	4·96	5·55
	8	−0·75	1·48	1·39	1·57
70	2	2·04	3·71	3·89	3·39
	4	−0·57	0·98	2·64	2·04
	8	0·59	3·46	5·07	5·84
80	2	5·34	7·48	4·88	6·33
	4	5·30	7·35	6·40	7·42
	8	4·27	8·65	7·78	7·65
90	2	6·66	10·60	11·15	8·87
	4	6·41	11·55	10·88	9·91
	8	9·61	11·74	14·07	12·99
100	2	11·05	16·01	15·74	15·90
	4	10·43	13·59	14·58	13·57
105	2	12·31	20·44	21·54	20·20
	4	18·94	27·51	25·91	28·91

Benzyl Alcohol

In these experiments a 3% (w/v) solution of benzyl alcohol was used. The temperature range covered was 60–105°C and the times of treatment were 2, 4, and 8 h. In addition, data were obtained for a treatment for 45 min at 80°C in 2% (w/v) benzyl alcohol, since these conditions have been recommended in practice. The results are given in Table III and are illustrated by Fig. 1.

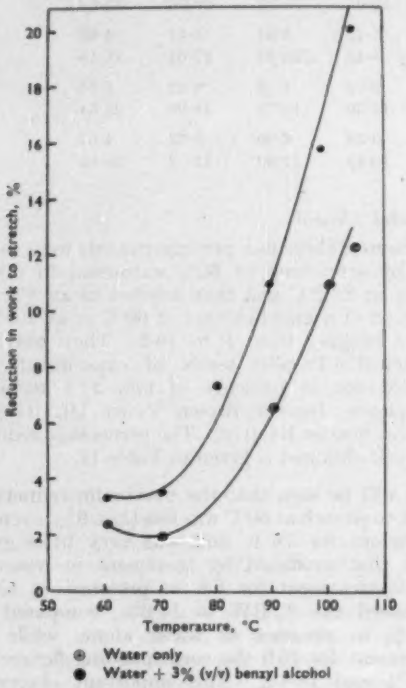

FIG. 1

Values for % RW after treatment in presence of benzyl alcohol were only very slightly greater than those obtained after treatment in water alone at temperatures up to 80°C. Above 80°C the values increased, those for treatment in aqueous solvent increasing more rapidly than those for treatment in water only. Temperature of treatment appeared to be more significant than time of treatment, at least at temperatures up to 100°C. Inclusion of dye in the system had no significant effect.

The greater increase in % RW in presence of benzyl alcohol (or butyl alcohol) at temperatures above 90°C is interesting and important. This is undoubtedly due to an effect of the solvent. If the solvent is completely removed from the fibre during washing subsequent to the treatment, the effect must be due to an irreversible change brought about by the solvent. At present it is not possible to give a complete explanation of this observation, which apparently has not been previously reported. It has been shown, however [5], that the resistance to extension of wool fibres stretched in aqueous solutions of n-propyl alcohol at room temperatures is lower than that of fibres stretched in water alone,

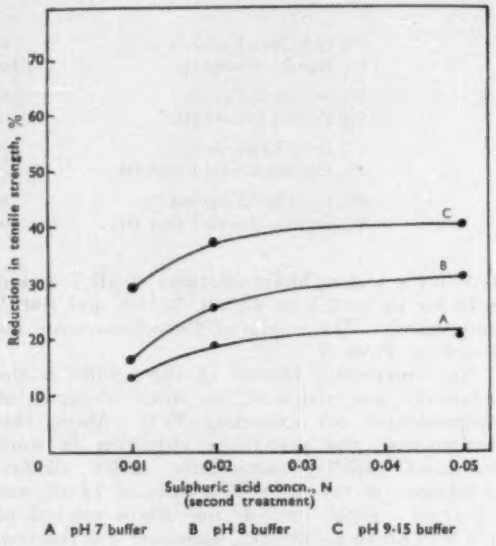

FIG. 2

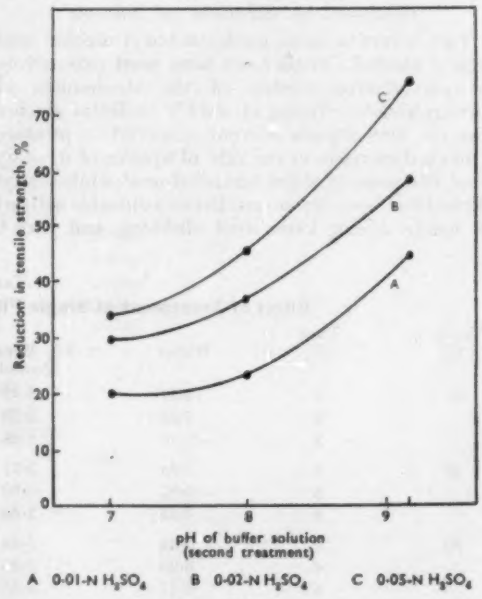

FIG. 3

TABLE IV

Effect of Treatment of Single Fibres in Water and in Benzyl Alcohol

Time (min)	Temp. (°C)	% Reduction in work to stretch 30% in Distilled water	2% (w/v) Benzyl alcohol	2% Benzyl alcohol + 2% Irgalan Grey BL	2% Benzyl alcohol + 8% Irgalan Grey BL
45	80	3·12	5·20	4·63	5·66

the maximum reduction being observed in 45% (w/v) solution of the solvent. This suggests that the alcohol–water mixture breaks more secondary bonds in the wool structure than does water alone. Similar fissions brought about at 100°C must, apparently, be irreversible. It may also be that the washing treatment given to the fibre does not remove all the adsorbed alcohol, so that the residual alcohol may weaken the wool. This effect, however, is likely to be small because no significant increase in % RW was observed in presence of benzyl alcohol at temperatures below 80°C.

The conditions of treatment used when obtaining the results given in Table III are, of course, quite different from those used in practice. The values for % RW after treatment in presence of 2% (w/v) benzyl alcohol for 45 min at 80°C, recorded in Table IV, suggest that, by using solvent-assisted dyeing methods at temperatures not exceeding 80°C, the extent to which adverse modification of the wool fibre occurs is less than that resulting from conventional dyeing procedures.

THE EFFECT OF TREATMENTS OF YARNS

Successive Treatments in Acid and in Alkaline Buffer Solutions

Hanks of yarn were treated in boiling solutions of sulphuric acid (0·01–0·05 N) and in buffer solutions of pH 7, 8, and 9·15, treatment being continued for 2 h in the sulphuric acid solutions and for 1 h in the buffer solutions. A further series of experiments was carried out at 105°C, treatment in acid solutions being continued for 30 min and treatment in buffer solution (pH 8 buffer only) for 15 min. Details of the experiments and the results obtained are given in Table V.

The tensile strength of yarn (measured on both 12-in. and 1-mm test lengths) treated in an acid

TABLE V

Effect of Successive Treatments on Tensile Strength and Elongation at Break of Dry Yarn

Treatment		Tensile strength (oz)		Extension at break (%)
First	Second	12-in. length	1-mm length	
		Treatments at 100°C		
Untreated yarn		57·2	67·4	37·0
0·01 N H_2SO_4	None	53·6	65·3	31·1
0·02 N H_2SO_4	None	49·1	62·9	33·0
0·05 N H_2SO_4	None	45·1	58·6	35·6
pH 7 buffer	None	51·1	66·6	32·7
pH 8 buffer	None	49·0	60·2	34·8
pH 9·15 buffer	None	40·1	53·5	32·4
pH 7 buffer	0·01 N H_2SO_4	49·3	59·5	29·1
0·01 N H_2SO_4	pH 7 buffer	45·6	51·9	28·1
pH 8 buffer	0·01 N H_2SO_4	47·5	56·4	26·8
0·01 N H_2SO_4	pH 8 buffer	43·8	53·1	26·2
pH 9·15 buffer	0·01 N H_2SO_4	40·1	48·2	20·4
0·01 N H_2SO_4	pH 9·15 buffer	33·2	38·2	17·3
pH 7 buffer	0·02 N H_2SO_4	46·2	57·0	28·4
0·02 N H_2SO_4	pH 7 buffer	40·5	52·0	23·3
pH 8 buffer	0·02 N H_2SO_4	41·8	56·1	22·9
0·02 N H_2SO_4	pH 8 buffer	35·8	40·2	21·0
pH 9·15 buffer	0·02 N H_2SO_4	35·6	41·3	23·2
0·02 N H_2SO_4	pH 9·15 buffer	23·6	26·1	12·0
pH 7 buffer	0·05 N H_2SO_4	46·1	54·1	21·6
0·05 N H_2SO_4	pH 7 buffer	37·6	47·4	22·2
pH 8 buffer	0·05 N H_2SO_4	38·5	43·3	17·9
0·05 N H_2SO_4	pH 8 buffer	30·9	38·3	16·6
pH 9·15 buffer	0·05 N H_2SO_4	34·0	37·6	19·3
0·05 N H_2SO_4	pH 9·15 buffer	13·4	19·9	10·6
		Treatments at 105°C		
0·01 N H_2SO_4	None	49·7	—	33·9
0·02 N H_2SO_4	None	50·8	—	34·0
0·05 N H_2SO_4	None	49·1	—	31·6
pH 8 buffer	None	45·2	—	26·6
pH 8 buffer	0·01 N H_2SO_4	42·6	—	29·2
0·01 N H_2SO_4	pH 8 buffer	38·6	—	25·7
pH 8 buffer	0·02 N H_2SO_4	44·8	—	28·8
0·02 N H_2SO_4	pH 8 buffer	35·2	—	17·7
pH 8 buffer	0·05 N H_2SO_4	38·9	—	27·0
0·05 N H_2SO_4	pH 8 buffer	23·4	—	10·4

solution and then in an alkaline solution was lower than that of the same yarn after the same treatments in the reverse order. This effect was observed in the case of treatments carried out at 100°C and at 105°C. The effect of the order of treatment increases with increase in the concentration of sulphuric acid and still more with increase in the pH of the alkaline solution. The general effect is illustrated in Fig. 2 and 3.

Figures for extension at break are included in Table V. It was observed that reduction in tensile strength was always accompanied by a reduction in extensibility and that the greater reduction in tensile strength observed when treatment in alkali followed treatment in acid was matched by a correspondingly greater reduction in extension at break.

The cystine and cysteine contents of the yarn samples were also determined. It was found that, although cystine was not removed from normal wool by treatment in acid solutions, some cystine was removed from wool that had previously been treated in alkaline solution. Similarly, more cystine was removed during alkaline treatment from wool previously treated in acid than from untreated wool (see Table VI).

TABLE VI

Sulphur Content of Treated Wool

Treatment		% Sulphur
First	Second	(as disulphide sulphur)
0·05 N H_2SO_4	None	2·97
pH 9·15 buffer	None	1·44
pH 9·15 buffer	0·05 N H_2SO_4	1·28
0·05 N H_2SO_4	pH 9·15 buffer	1·02
Untreated wool		3·02

It is not possible at this stage to account satisfactorily for these observations, but a tentative explanation may be put forward. Several workers consider that the tensile properties of wool are profoundly affected by the –S–S– linkages. Fission of these bonds causes a weakening of the fibre. It is probable that pretreatment of the wool will make the fibre more susceptible to attack by alkali, largely by increasing the accessibility to the reagent. Alkalis will, therefore, attack acid-treated wool more rapidly than untreated wool, and consequently more –S–S– linkages will be broken in the acid–alkali sequence of treatments than in the alkali–acid one, since acids do not break –S–S– linkages. It is of interest to note, however, from the figures given in Table VI that more disulphide sulphur is lost by treatment in pH 9·15 buffer followed by treatment in 0·05-N H_2SO_4 than by treatment with pH 9·15 buffer alone, indicating that the acid does remove some –S–S– linkages. This is probably due to removal of a particular fraction of degraded keratin, rather than fission of –S–S– linkages. Further work is in hand to examine this hypothesis in greater detail.

Successive Treatments in Dye Solution and in Sodium Carbonate Solution

The study of the influence on the tensile strength of wool yarn of treatment in acid and alkaline solutions was extended to include the effect of conventional dyebaths on yarn previously treated in alkaline media and the effect of treating dyed yarn in the same alkaline solutions, to see if the order of treatments is of practical as distinct from theoretical significance. For this reason, a 0·01 g/l.

TABLE VII

Percentage Reduction in Tensile Strength of Wet Yarn on Dyeing and Treatment in Alkali

I Treatment in dyebath
II Treatment in sodium carbonate solution (0·01 g/l; pH 9·4 → 8·0)
III Treatment in pH 8 buffer
Effect of II alone = 11·4%
Effect of III alone = 25·4%

Dyebath	I	Sequence I—II	Sequence II—I	Sequence I—III	Sequence III—I
Blank dyebath (final pH 7·0)	13·1	19·1	17·3	32·3	29·1
2% Carbolan Blue BS	13·3	15·4	16·4	30·6	30·0
2% Carbolan Violet 2RS	13·6	14·8	13·6	29·5	28·1
2% Carbolan Green G125	13·1	13·1	16·7	30·8	28·1
Blank dyebath (final pH 6·5)	13·1	14·8	16·7	38·6	35·7
2% Irgalan Red 3G	15·0	17·5	14·5	40·7	38·0
2% Irgalan Brown Violet DL	15·0	17·5	14·1	40·7	36·7
Blank dyebath (final pH 2·8)	12·7	15·0	21·1	33·5	29·7
2% Orange II (Comm.)	10·1	14·1	17·9	32·3	29·9
2% Orange II (Pure)	10·3	15·4	19·4	33·3	29·1
Blank dyebath (final pH 2·1) 100°C	20·7	28·1	29·5	60·6	42·6
2% Neolan Blue GG 100°C	18·4	29·9	27·2	70·2	50·4
Blank dyebath (final pH 2·1) 60°C	5·1	7·2	9·3	25·3	25·1
2% Neolan Blue GG 60°C	8·4	9·3	10·8	26·6	27·6
Butyl alcohol 60°C	10·0	12·9	12·2	24·9	24·7
2% Irgacet Scarlet RL 60°C	9·3	13·5	14·5	28·7	29·7
Butyl alcohol 100°C	13·5	18·8	21·5	40·1	33·7
2% Irgacet Scarlet RL 100°C	17·1	21·5	23·0	39·2	36·2

solution of sodium carbonate was used in preference to a pH 8 buffer solution for these experiments.

Dyeing methods used included— (*a*) strongly acid dyebaths (pH 2), as used for 1 : 1 premetallised dyes; (*b*) acid dyebaths (pH 2·8), as for level-dyeing acid dyes; (*c*) neutral dyebaths (pH 6–7), as used for neutral-dyeing acid dyes and neutral dyeing 2 : 1 premetallised dyes. In addition to conventional dyebaths, an 8% (v/v) aqueous solution of n-butyl alcohol was used.

In all cases, except two, dyeing was carried out under reflux at 100°C, using a solution : material ratio of 100 : 1, as were treatments in pH 8 buffer solution and sodium carbonate solution. Dyeing was continued for 2 h and treatment in alkaline solutions for 1 h. The samples were washed between treatments and after the final treatment, as in the previous experiment.

In this series of experiments, tensile strength was determined on 10-in. lengths of wet yarn, as measurements on wet yarn have been claimed to be preferable to tests on dry yarn for the detection of slight damage. The results obtained are listed in Table VII.

The effect of the conventional dyeing treatments was as would be expected from the dyeing conditions; significantly greater reduction in tensile strength occurred under strongly acid conditions at pH 2. The greater loss in strength observed with a pH 8 buffer than with 0·01 g/l. sodium carbonate solution is no doubt due to a specific ion effect.

The total reduction in tensile strength caused by two successive treatments was considerably less than the sum of the reductions produced by the individual treatments, except when dyeing was carried out under strongly acid conditions (pH 2). Even in this case the total reduction in tensile strength was only significantly greater than the sum of the effects of the separate treatments when pH 8 buffer was used in the alkaline treatment.

The sequence of treatments was significant only when strongly acid dyeing conditions and pH 8 buffer were used. In this case, as when an acid–alkali sequence was used, a greater reduction in tensile strength was observed when treatment in an acid dyebath preceded treatment in alkali.

* * *

One of us (J.E.) is indebted to the International Wool Secretariat for a scholarship which enabled him to take part in this investigation.

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(*MS. received 19th May 1961*)

References

[1] Hirst, H. R., and King, P. E., J.S.D.C., **53**, 198 (1937).
Liu, W. T., Speakman, J. B., and King, P. E., *ibid.*, **55**, 185 (1939).
Mazingue, G., Outreman, P., and Overbèke, M. van, *Bull. Inst. Text. France*, No. 42, 23 (1953).
Farnworth, A. J., *Textile J. Australia*, **27**, 233 (1952).
Peryman, R. V., J.S.D.C., **64**, 283 (1948); **70**, 83 (1954); **71**, 165 (1955).
Lees, K., and Elsworth, F. F., *Proc. Int. Wool Textile Res. Conf. Aust.*, 1955, C-163.
Lees, K., Peryman, R. V., and Elsworth, F. F., *J. Textile Inst.*, **51**, T717 (1960).
[2] Kärrholm, M., and Lindberg, J., *Text. Research J.*, **26**, 528 (1956).
Kärrholm, M., *J. Textile Inst.*, **51**, T1323 (1960).
Medley, J. A., and Ramsden, D. K., *ibid.*, **51**, T1311 (1960).
Peters, L., Stevens, C. B., Budding, J., Burdett, B. C., and Sykes, J. A. W., J.S.D.C., **76**, 543 (1960).
[3] Peters, L., and Stevens, C. B., *ibid.*, **72**, 100 (1956).
[4] Beal, W., Bellhouse, E., and Dickinson, K., *ibid.*, **76**, 333 (1960).
[5] Atkinson, J. C., Filson, A., and Speakman, J. B., *Nature*, **184**, 444 (1959).

Discussion

Dr. G. H. LISTER: Recently I have been interested in the formation of new cross-links from hydrolysed or reduced cystine bonds in wool, and conflicting results were obtained in comparing laboratory experiments with bulk trials.

A considerable amount of work was carried out to discover the reason for the discrepancies and proof was eventually obtained that the key was to be found in the drying conditions. High humidity appears to be essential to ensure rapid re-oxidation of two thiol groups to cystine. In the laboratory, where quick drying occurs, two thiol groups were unable to re-oxidise to re-form cystine bonds. In bulk practice, however, where conditions of high humidity were maintained for much longer periods, oxidation could occur during drying. It would be interesting to know whether the authors had considered this factor.

A second contribution to cross-linking was found to be the state of tension in which the wool was held during drying. Evidence is available that in bulk experiments "setting" of dyed wool is more likely to occur during drying than during dyeing.

Mr. OLDFIELD: In the experiments described in this paper, the yarn was dried in a Mitchell dryer without tension, after being squeezed to remove surplus water. Single fibres were never dried but were kept immersed in distilled water.

Mr. W. BEAL: Fig. 1 on p. 730 gives a comparison between water and water plus 3% (v/v) benzyl alcohol. I would suggest that a third curve should be shown in which the benzyl alcohol concentration is varied to cover the conditions used in practice, viz.,

4% (v/v) at 60°C; 3% (v/v) at 70°C; 2% (v/v) at 80°C and 0·7% (v/v) at 90°C.

This curve would probably correspond much more closely to that for water alone.

Dr. STEVENS: I agree that it would be of interest to do this, but lack of time has prevented our including additional information.

FRIDAY AFTERNOON, 22nd SEPTEMBER 1961

Chairman—Mr. R. C. OAKLEY

The Hydrolysis of Reactive Dyeings

J. BENZ

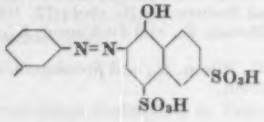
Twelve reactive dyes were synthesised containing the same chromophore but different reactive systems and different bridge members. These dyes were applied to mercerised cotton at approximately standard depth and the effects on the dyeings of alkaline and acid hydrolysis were studied. Increasing reactivity of dichloro- and trichloro-pyrimidyl dyes is accompanied by a growing tendency to acid and, more particularly, alkaline hydrolysis. The position at which saponification occurs depends on the nature of the bridge member. In a second series of dyes, various reactive systems were combined with the same chromophore through an imino group; no general relation between reactivity and tendency to hydrolysis could be established for these dyes.

Introduction, and Scope of Examination

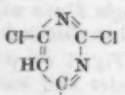
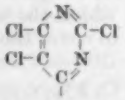
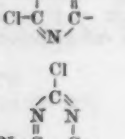
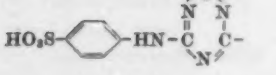
Reactive dyes may be defined as dyes which react with the textile substrate to form a homopolar linkage. Of the types of fibre dyed commercially with reactive dyes, cellulose ranks first in interest and importance.

We decided to examine the hydrolysability in aqueous alkaline and aqueous acid media of dyeings on cellulose produced with selected reactive dyes. Our main objective was to examine the dependence of hydrolysability on the constitution of the dyes, but we also sought a relation between hydrolysability and reactivity.

For this purpose, a series of dyes was synthesised containing the same chromophore—



This chromophore was combined with different reactive systems and in some instances the bridge member also was varied—

Reactive system		Linkage	Dye
Chlorinated pyrimidines			
Dichloropyrimidyl radical		–NH–	I
		–O–	II
		$-OCH_2-$	III
Trichloropyrimidyl radical		–NH–	IV
		$-N(CH_3)-$	V
		–O–	VI
Chlorinated triazines			
		–NH–	VII
		–NH–	VIII

Carboxylic acid radicals

$ClCH_2CH_2CO-$	–NH–	IX
$CH_2=CHCO-$	–NH–	X
$CH_3-\underset{Cl}{C}=CHCO-$	–NH–	XI

Sulphuric acid ester of β-hydroxyethyl sulphone

$HO_3S-OCH_2CH_2SO_2-$	XII

As written here, the formulae of the two pyrimidyl radicals presuppose that trichloro- and tetrachloro-pyrimidine have previously exchanged their halogen atoms in the 4-position, which seems very probable from the work of Ackermann [1].

Experimental Methods

The twelve reactive dyes were applied to mercerised cotton at approximately standard depth. Dye VII, of the dichlorotriazinyl type, was fixed at 20°C with the addition of soda ash, as in the pad–batch process, and the others were fixed by dry heat. The dyeings were carefully washed and the fixation yields determined before the dyeings were hydrolysed.

The hydrolysing conditions were selected independently of practical considerations, i.e. fastness to manufacturing processes and wear. The treatments were intentionally far more rigorous than any to which dyed fabrics are normally exposed, firstly, because it was desired to remove a substantial proportion of the dye by hydrolytic cleavage and, secondly, because these severe conditions bring out more clearly the distinctive differences between the individual systems. Alkaline hydrolysability was tested by mechanical agitation of the dyed sample for 6 h in a 2% soda ash solution at 95°C, the pH of the solution being approx. 11. To prevent reduction taking place, a small amount of *m*-nitrobenzenesulphonic acid was added. Acid hydrolysability was similarly tested by agitating the sample for 6 h in a solution at 70°C, buffered to pH 3·0. Repeated tearing tests of both untreated and hydrolysed dyeings showed that no measurable damage to the fabric occurs under these conditions.

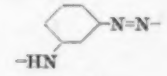
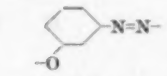
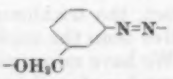
To study the mechanism of hydrolysis, the cleavage products were analysed chromatographically. For most of the dyeings, the chromatograms showed with reasonable certainty whether the linkage between the reactive system and the

cellulose or that between the chromophore and the reactive system had undergone hydrolysis. Where only a very small fraction of the dyeing was hydrolysed, chromatography was not employed. For the quantitative examination of hydrolysis, we dissolved the untreated and the hydrolysed dyeings in sulphuric acid, diluted the solutions with water, and compared the extinction coefficients. This method, developed by Michie and Thornton [2] for vat dyeings, was first employed for reactive dyeings by Dawson, Fern, and Preston [3].

The content of the cleavage product solutions was determined by measuring the optical densities. When the solute was more or less homogeneous, consisting either of saponified dye or of chromophore, the cleavage product was compared with corresponding solutions of known concentration. The amount of dye remaining on the fibre plus that found in the cleavage product was approximately equal to the amount of dye in the initial dyeing. With some dyeings which bled heavily in the alkaline bath, the sum of the two amounts was not quite equal to the dye content of the original dyeing, presumably because some dye is destroyed in spite of the presence of oxidising agent in the bath. Where the solute was heterogeneous we were obliged to rely mainly on the determinations of the amount of dye remaining on the fibre. To check the results, the hydrolysed dye was applied to wool. Comparison of these dyeings with the optical measurements showed that the measured values, while they cannot be claimed to be entirely accurate, do express fairly well the relations between the individual dyes.

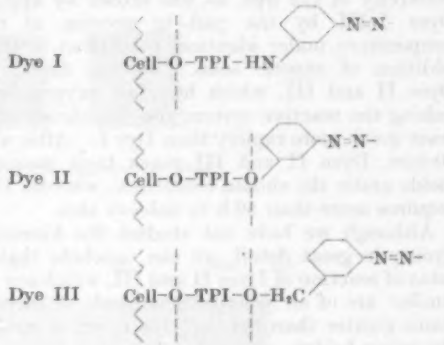
Alkaline Hydrolysis

Alkaline hydrolysis of dyeings of three dichloropyrimidyl dyes in which the reactive system is linked to the chromophore through different bridge members gave the following results—

Dye		Extent of hydrolysis (%)
I		5
II		20
III		33

It will be noted that the dye with an imino bridge between the reactive system and the chromophore gives dyeings of much better stability to alkali than those of dyes with oxygen bridges.

Chromatographic examination of the dissolved cleavage products revealed that with Dye I saponification takes place chiefly between the cellulose and the reactive system (see Fig. 1). By contrast, the cleavage product from the dyeing of Dye II contains mostly chromophore, i.e. the coupling product of *m*-aminophenol and 1-naphthol-4,6-disulphonic acid. This was evident when the chromatograms of the cleavage product, the chromophore, and a mixture of the two compounds were compared. The mixture of cleavage product and chromophore could not be separated under the various chromatographic conditions at which it was examined. The cleavage product of the dyeing of Dye III contains similar amounts of chromophore and of dye which has retained the pyrimidyl radical. For chromatography we used throughout aqueous alkaline eluents. The chromophore is adsorbed much less on paper and on talc than the dye, which contains the pyrimidyl radical and hence is of considerably greater molecular weight.



TPI = Divalent radical of trichloropyrimidine

FIG. 1— Saponification of dyeings of dichloropyrimidyl dyes

These results are easily understood if trichloropyrimidine is regarded as the chloride of barbituric acid. In Dye I the reactive system is linked to the chromophore through an acid amide linkage. It is to be expected that this linkage will be more stable to alkali than the ester linkage between the reactive system and cellulose. Matters are different with Dye II: in dyeings of this dye, the pyrimidyl radical is combined on one side to the chromophore through a phenol ester linkage, while on the other side the pyrimidine ring is esterified with an aliphatic hydroxy group of the cellulose. It is not surprising that, on alkaline attack, the ester linkage with the phenol is the first to be saponified, since phenol esters are more easily saponified with alkalis than the corresponding esters with primary aliphatic alcohols.

In the dyeing of Dye III, the pyrimidine ring is again esterified with the cellulose and with the chromophore. Both are esters with aliphatic hydroxy groups. They should therefore possess similar stability to alkalis if we can assume, as is highly probable, that cellulose reacts mainly with the primary hydroxy groups. In fact, chromatography of the cleavage product does show similar amounts of chromophore and saponified reactive dye. It was to be expected that the ester linkage of the pyrimidine ring and chromophore, activated by the adjacent phenyl nucleus, would be more readily saponified by alkali than the dye–fibre linkage. As we did not determine the exact ratio of the two constituents in the cleavage product, it is possible that our test result also agrees quantitatively with these expectations.

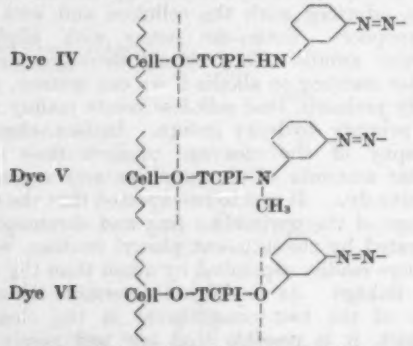
Certainly the presence of chromophore in the cleavage product is not due to further saponification of an appreciable amount of the saponified dye formed by hydrolysis of the cellulose linkage. Throughout the hydrolysis the ratio of the two constituents did not vary sufficiently to be visible in the chromatograms.

The influence of the type of linkage between the reactive system and the chromophore on the alkaline hydrolysability of the dyeings is very marked in these three examples. The bridge member between the reactive component and the chromophore also has a decisive influence on the reactivity of the dye, as was shown by applying Dyes I–III by the pad–jig process at room temperature under identical conditions, with the addition of caustic soda. It was found that Dyes II and III, which have an oxygen bridge linking the reactive system and the chromophore, react much more rapidly than Dye I. After about 30 min, Dyes II and III reach their maximum yields under the chosen conditions, whereas Dye I requires more than 50 h to achieve this.

Although we have not studied the kinetics of dyeing in great detail, we can conclude that the rates of reaction of Dyes II and III, which are very similar, are of an order of magnitude at least two times greater than that of Dye I, which contains the imino bridge.

The results of alkaline hydrolyses of the dyeings of the trichloropyrimidyl dyes (IV, V, VI) are illustrated in Fig. 2. Here again the imino and, to a somewhat smaller extent, the methylimino linkage between the reactive system and the chromophore give dyeings of better alkaline stability than those of dyes containing the corresponding phenol ester linkage.

Chromatographic examination of the cleavage products enabled us to determine the position of hydrolytic cleavage from the fibre, as shown in Fig. 3. With the dyeings of Dyes IV and V, which are combined with the reactive radical through an imino and a methylimino bridge, respectively, hydrolysis in an alkaline medium takes place predominantly at the dye–cellulose linkage. In contrast, with Dye VI it is chiefly the link between the pyrimidine ring and the chromophore that is split. Dyes IV and VI behave in exactly the same way as the dichloropyrimidyl derivatives of corresponding structure.



TCPI = Divalent radical of tetrachloropyrimidine

FIG. 3— Saponification of dyeings of trichloropyrimidyl dyes

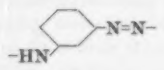
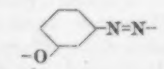
The bridge member has a marked effect on the reactivity of the trichloropyrimidyl dyes. By replacing the imino bridge in products of the type of Dye IV by a methylimino group, as in Dye V, the reactivity is substantially increased. Fig. 4 illustrates the reactivity of another pair of corresponding dyes with an imino and a methylimino group, respectively. These two dyes were applied by the pad–jig process with caustic soda at room temperature. After the times indicated, cuttings were taken and washed off. The dye from *N*-methyl-J-acid attains its maximum fixation yield after about 40 min, whereas more than 50 h are necessary for the J-acid dye.

Having found that replacement of the imino group by the methylimino group greatly increases the reactivity of trichloropyrimidyl dyes, we considered that the reactivity of dyes of this type would depend on the basicity of the amino group to be condensed with tetrachloropyrimidine. It is not easy to prove this assumption correct by dyeing methods alone, as in most cases other properties of the dye, e.g. substantivity and salt sensitivity, which can also affect the dyeing behaviour, are modified simultaneously with the change in the basicity of the amino group to be condensed. Nevertheless, it can be assumed that the differences in reactivity of the individual members of a series of trichloropyrimidyl dyes, all having the reactive radical linked with the chromophore through an imino bridge, are due at least partly to the varying basicity of the condensed amino group.

When the hydrolysability of the dyeings in an alkaline medium is compared with the reactivity of the corresponding dichloro- and trichloropyrimidyl dyes, it will be observed that the hydrolysability of the dyeing increases with increasing reactivity of the dye (Table I). If this

TABLE I

Hydrolysis of Pyrimidyl Reactive Dyes

Linkage	Extent of hydrolysis (%)			
	Dichloro-pyrimidyl		Trichloro-pyrimidyl	
	I	5	IV	7
	II	20	VI	45

conclusion is correct, the trichloropyrimidyl dyes will be more reactive than the analogous dichloropyrimidyl ones. We have measured the reactivity of a considerable number of analogous pairs of such dyes and our findings support this contention.

This is illustrated by the example in Fig. 5. Equal amounts of analogous salt-free dyes of the indicated formulae were applied by the pad–batch process at 25°C under identical conditions, i.e. with caustic soda and 15-h storage at room temperature. The depth of the trichloropyrimidyl dyeing is 2½ times greater than that of the corresponding dichloropyrimidyl dyeing.

Alkaline hydrolysis of dyeings of the two triazinyl dyes (VII, VIII) resulted in 24% (Dye VII) and 38% (Dye VIII) hydrolysis. Dye VII was applied by the pad–batch process at 20°C with

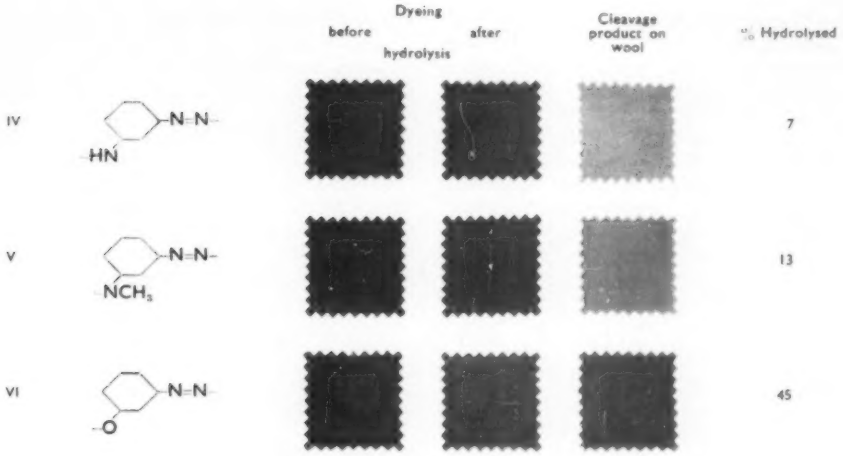


FIG. 2— Alkaline hydrolysis of dyeings of trichloropyrimidyl dyes

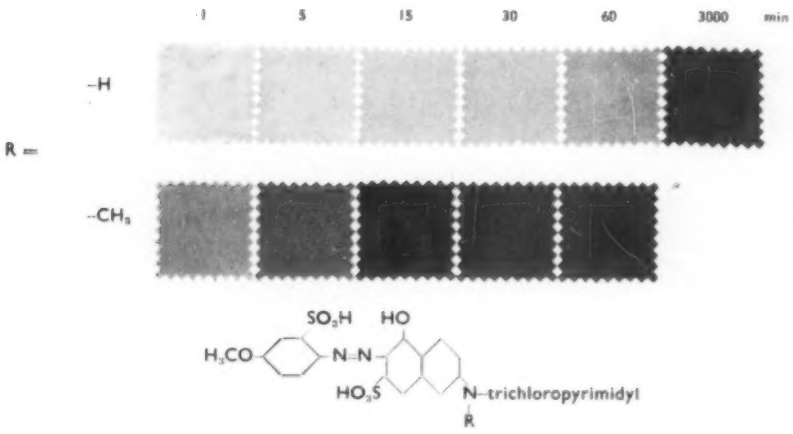


FIG. 4— Reactivity of trichloropyrimidyl dyes

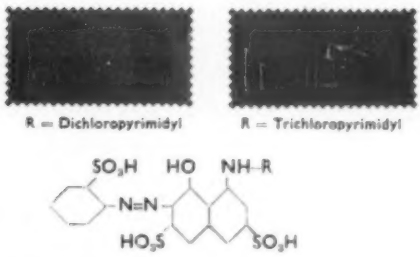
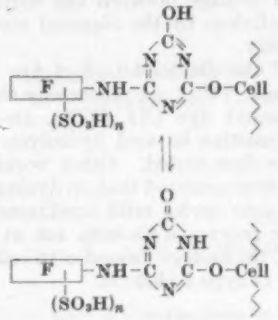


FIG. 5— Reactivity of analogous dichloropyrimidyl and trichloropyrimidyl dyes

soda ash. It must be remembered that dichlorotriazinyl dyes, which possess two reactive halogen atoms, can react differently with cellulose, depending on the conditions of application. Preston and Fern [4], and Elöd and Nakahara [5], have shown that three different linkages can be formed by dichlorotriazinyl dyes on cellulose. This aspect will be dealt with briefly in the section on acid hydrolysis.

Under the severe conditions of alkaline hydrolysis adopted, it is probable that dyeings of dichlorotriazinyl dyes, independently of the method of application, are converted into one of the following two tautomeric forms—

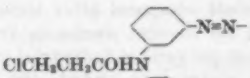
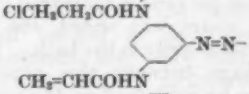
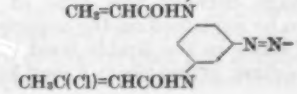


(F is the chromophore of the dye)

The enol form, which is probably the predominant one in an alkaline medium, can be expected to show high alkaline stability, owing to its aromatic character. An acid medium should favour formation of the lactam form. An important advantage of the dichlorotriazinyl dyes is the combination of very high reactivity with relatively good stability to alkaline hydrolysis. As a result they can be subjected in many dyeing processes to conditions far more rigorous than those required for the maximum fixation yield without the dyeing being stripped off the fibre.

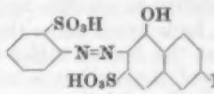
The dyeing of the analogous monochlorotriazinyl dye is less stable to alkali. However, these findings cannot be considered generally applicable, for the alkaline stability of monochlorotriazinyl dyes is clearly dependent on the nature of the second colourless substituent on the triazine ring. Chromatography of the cleavage product of the dyeing of the monochlorotriazinyl dye showed that the dye–fibre linkage had been broken.

Three of the dyes tested contained a reactive carboxylic acid radical combined with the chromophore through a carboxylic acid amide link. Alkaline hydrolysis indicated that the dyes containing the β-chloropropionyl (IX) and the acryloyl radical (X) give dyeings of poor alkaline stability, compared with the analogous type containing the β-chlorocrotonoyl radical (XI), as shown at the foot of the previous column.

Dye		Extent of hydrolysis (%)
IX		61
X		63
XI		4

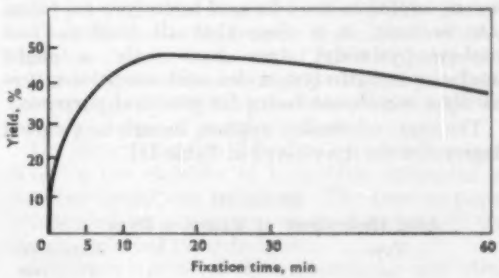
Comparison with the dyeings of analogous dyes containing other acyl radicals, notably the dichloro- and trichloro-pyrimidyl radicals, shows that the dyeings of the β-chloropropionyl and the acryloyl dyes are very sensitive to alkali.

The reactivities of these three reactive systems have been compared by preparing dyeings with



where R = $-COCH_2CH_2Cl$, $-COCH=CH_2$, or $-COCH=C(Cl)CH_3$. Compared with the dichlorotriazinyl or the vinyl sulphone dyes, these three are of low reactivity. Accordingly, they were applied by the pad–jig process from a hot bath, i.e. at 90°C, with soda ash. The dyes containing the β-chloropropionyl radical and the acryloyl radical react at approximately the same rate. This supports the view of Zollinger [6] that β-chloropropionyl dyes split off primary hydrogen chloride in an alkaline medium, the resulting acryloyl derivative forming an addition compound with the cellulose. The dye containing the β-chlorocrotonoyl group is rather more reactive than the other two.

The rule that the hydrolysability of the dyeings increases with increasing reactivity of the dye holds good only when the reactive system is identical. As the above examples show, it is not true of analogous dyes with different reactive systems. The dyes containing the β-chloropropionyl and the acryloyl radical show comparatively low reactivities but, on the other hand, their dyeings are very susceptible to alkaline hydrolysis. As a result, the optimum range of fixation conditions is rather limited in these systems. This is illustrated by Fig. 6. The dye from orthanilic acid and *N*-acryloyl-J-acid was dyed by the pad–jig process and the yield plotted as a function of fixing time. The fixing bath, at 90°C, contained calcined sodium sulphate, caustic soda, and a little *m*-nitrobenzenesulphonic acid. After about 15 min



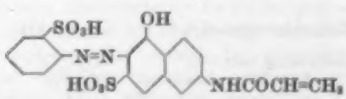
Dye: 

FIG. 6—Effect of fixation time on yield of reactive dye containing an acryloyl radical

treatment, the dyeing reached its maximum depth. If fixation was continued the dyeing began to lose depth as a result of alkaline hydrolysis. After 60 min, i.e. four times the time required to obtain maximum depth, it was already about 20% lighter. Dyes whose yield depends in such great measure on the fixing conditions give little assurance of consistent results in practical work.

The final dye tested was a vinyl sulphone derivative (XII). Of all the types of dye examined, the sulphuric acid ester of β-hydroxyethyl sulphone has the lowest stability to alkaline hydrolysis, the dyeing being 97% hydrolysed under the conditions used. Washing at the boil is sufficient to cause partial hydrolysis of these dyeings when soda is included in the bath. At the same time, this sensitivity to alkali is the basis for the good dischargeability of this type of dye. After printing with a strong caustic alkali paste and steaming, the hydrolysed dye can be completely removed from the fibre. In the alkali-stable dyeings of the pyrimidyl and triazinyl types of dye, a residue of dye linked with the cellulose through the reactive radical is always left on the fibre. If it is a clear white it is not objectionable, but very often the remaining amines tend to become brown on exposure to light.

Acid Hydrolysis

Table II shows the extent of acid hydrolysis of the dichloro- and trichloro-pyrimidyl dyes.

TABLE II
Acid Hydrolysis of Pyrimidyl Dyes

Type		Extent of hydrolysis (%)
Dichloropyrimidyl	Dye I	0·3
	Dye II	2·0
	Dye III	1·3
Trichloropyrimidyl	Dye IV	0·4
	Dye V	0·7
	Dye VI	1·8

The tendency to acid hydrolysis increases within these two series to about the same degree as the tendency to alkaline hydrolysis; it increases with increasing reactivity of the dye. When the very severe conditions used for acid hydrolysis are taken into account, it is clear that all dichloro- and trichloro-pyrimidyl dyes have only a slight tendency to hydrolyse under acid conditions; it is hardly a significant factor for practical purposes.

The same conclusion applies, though to a varied degree, for the dyes listed in Table III.

TABLE III
Acid Hydrolysis of Reactive Dyes

Type		Extent of hydrolysis (%)
Monochlorotriazinyl	Dye VIII	1·9
Containing reactive carboxylic acid radical	Dye IX	2·5
	Dye X	2·3
Vinyl sulphone	Dye XII	0·1

The behaviour of the dye containing the sulphuric acid ester of β-hydroxyethyl sulphone is interesting. Its dyeings show unusually high resistance to acid hydrolysis. The characteristics of this type of dye are such that the dye–fibre linkage is rather more stable than the glucoside linkages of the cellulose. Bohnert [7] succeeded in reducing dyeings of a vinyl sulphone dye by acid hydrolysis sufficiently to isolate the compound of the dye and glucose. At the same time he was able to react the dye with glucose and establish the identity of the resulting compound with the reduction product, thus obtaining conclusive proof of the homopolar linkage between the vinyl sulphone dye and cellulose by the classical methods of organic chemistry.

The dyeings of the dichlorotriazinyl dye (VII; extent of hydrolysis, 14%), and especially that of the β-chlorocrotonoyl dye (XI; 85%), are considerably more sensitive to acid hydrolysis than those of the other dyes tested. Other workers in this field [4, 5] have demonstrated that, in dyeing with dichlorotriazinyl dyes under mild conditions, e.g. in the pad–batch process with soda ash at 20°C used in this work, the linkage formed with cellulose is predominantly of type I (Fig. 7).

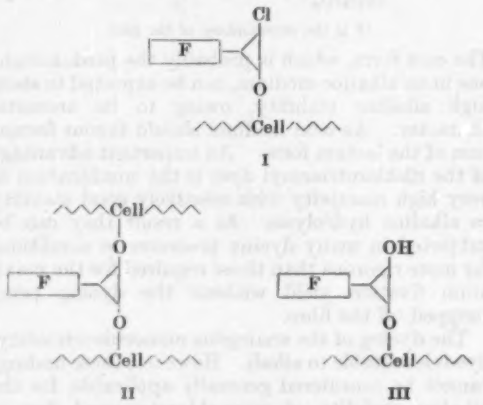


FIG. 7—Types of linkage between dichlorotriazinyl dyes and cellulose

Under more rigorous fixing conditions, e.g. in presence of strong alkalis and, above all, at higher temperatures, the formation of type II and type III linkages is promoted. Of the three types of linkage, I and II are comparatively stable to acid hydrolysis. Type III, formation of which is largely suppressed in the present work by the choice of application conditions, is easily hydrolysed under acid conditions.

The dyeing of the β-chlorocrotonoyl dye is extremely sensitive to acid. This was apparent from the result observed after these dyeings had been stored for several weeks in an acidic atmosphere such as prevails in industrial cities: when the fastness to water was tested, the dyeings were found to bleed heavily in the bath. The instability of the linkage between this type of dye and cellulose can be explained on the assumption that addition of water to the double bond takes place in an acid medium, giving rise to a semi-ketal which

is converted into a derivative of acetoacetamide by the action of acid (Fig. 8). In fact, the cleavage product formed by acid hydrolysis of dyeings of β-chlorocrotonoyl dyes is identical with the corresponding dye with the acetoacetic amide grouping produced by synthesis.

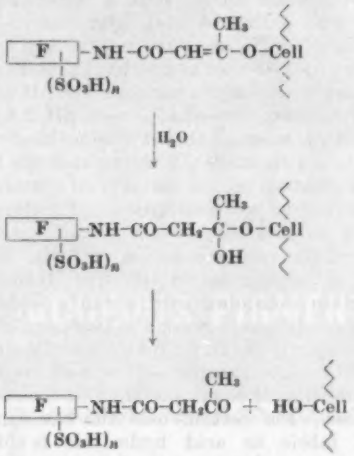


FIG. 8—Effect of acidic conditions on linkage between a β-chlorocrotonoyl dye and cellulose

Conclusions

With the aid of some dichloro- and trichloropyrimidyl dyes, it has been shown that the reactivity of the dye and the hydrolysability of the dyeings are dependent to a great extent on the bridge member between the chromophore and the reactive system. Within these series, increasing reactivity of the dye is accompanied by a growing tendency to acid and, more particularly, alkaline hydrolysis. With dyes having oxygen bridges, saponification of the dyeings in an alkaline medium occurs chiefly between the reactive system and the chromophore, while with dyeings of dyes containing imino or methylimino bridges the linkage between the reactive system and the cellulose is hydrolysed.

In a second series of dyes, various reactive systems were combined with the same chromophore through an imino group. Here no general relation between reactivity and the tendency to hydrolysis could be established. There is evidence that the dyeings of highly reactive dyes tend to be rather easily hydrolysed either in acid or in alkaline medium but, on the other hand, it was found that dyeings of some dyes with comparatively slow rates of reaction, e.g. those of the β-chlorocrotonoyl and β-chloropropionyl types, are also very susceptible to hydrolysis.

* * *

Thanks are due to Dr. O. Thumm, who carried out the tests, and to Dr. M. Capponi, Dr. H. Ruckstuhl, and Mr. A. Barthold for their co-operation.

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(*MS. received 6th September 1961*)

References

[1] Ackermann, H., Lecture to the German Association of Textile Chemists and Colourists, Baden-Baden, 5th May 1961.
[2] Michie, A. G. H., and Thornton, R., *J.S.D.C.*, **69**, 629 (1953).
[3] Dawson, T. L., Fern, A. S., and Preston, C., *ibid.*, **76**, 210 (1960).
[4] Preston, C., and Fern, A. S., *Chimia*, **15**, 177 (1961).
[5] Elöd, E., and Nakahara, Y., *Melliand Textilber.*, **41**, 567 (1960).
[6] Zollinger, H., *Angew. Chem.*, **73**, 125 (1961).
[7] Bohnert, E., Lecture to the German Association of Textile Chemists and Colourists, Baden-Baden, 5th May 1961.

Discussion

Mr. I. D. RATTEE: There are considerable dangers in drawing general conclusions from measurements of hydrolysis using:

1 single chromophores
2 single hydrolysis pH values
3 single buffer systems at any one pH.

The results with the chromophore used in Dr. Benz's work show that the differences in the extent of hydrolysis of dyes bearing different reactive systems on the same chromophore can be less than differences between dyes bearing the same reactive system. For example, Dye X shows a high degree of alkaline hydrolysis, but many acrylamido dyes show very high resistance to alkaline hydrolysis and compare with the esterifying dyes in this respect.

Secondly, not only does the stability of the dye–fibre bond formed by dyes derived from cyanuric or barbituric acid vary with pH on the acid side, but the relative hydrolysis levels of different dyes vary, so that at one pH Dye A may show more hydrolysis than Dye B while at another pH the position is completely reversed.

This latter effect is also shown if the composition of the buffer used to produce a particular pH is changed. With, for example, Dyes VII and VIII, a phthalate–HCl buffer giving pH 2·8 shows hydrolysis levels which are 45% and 20% less, respectively, than with an acetic acid buffer at the same pH under the conditions used by Dr. Benz.

Thus the use of hydrolytic techniques, while a valuable tool for research on bond stability and reactivity, presents many highly complex problems, not the least of which is the interpretation of the results in terms of practical effects.

Dr. BENZ: As yet, little detailed work has been done on the stability to hydrolytic influences of reactive dyeings on cellulose. The present paper is intended as a contribution to the study of the factors involved in hydrolysis.

Within a series of dyes containing the same reactive system, the tendency to hydrolysis of the dyeings is determined by the bridge member and the chromophore. In order to examine the influence of different reactive systems on the hydrolysability, it is therefore necessary to use dyes containing the same chromophore and the

same bridge member. This principle must also be observed in testing the influence of the bridge member. Comparison of the hydrolysability of the dyeing of any one dye containing the reactive system A with that of any other dye containing the reactive system B is therefore of little value.

Some of the results obtained with our series of experimental dyes have been checked with dyes of other series having different chromophores, and the same tendencies have been observed. Thus we found in our alkaline hydrolysis tests that dyeings of acrylamido dyes are far less stable than those of the corresponding dichloropyrimidylamino and trichloropyrimidylamino dyes. Wegmann (*Melliand Textilber.*, **39**, 1006 (1960)) has shown that dyeings of β-chloropropionylamido dyes are relatively easily hydrolysed in an alkaline medium; this must also be true for dyeings of the acrylamido dyes, since they have the same structure.

The stability of reactive-dyed cellulose is dependent to a marked degree on pH. Zollinger (private communication; paper in preparation) has examined the initial rate of hydrolysis of dyeings on cellulose of various types of reactive dyes and has found that each type has a sharply defined stability maximum at a characteristic pH. At pH below and above the stability maximum the rate of hydrolysis increases rapidly. The stability maxima for two dyes of different types may lie at significantly different pH. In view of these findings it is possible that the relation between the stabilities of dyeings of different types of reactive dyes may vary considerably at different pH.

Mr. Rattee's statement that under otherwise identical conditions the stability of a reactive dyeing can be dependent on the composition of the buffer is interesting. We have not studied this aspect of the problem. To do so, it would be necessary to take into account the buffer capacity of the mixture used. With a buffer of potassium hydrogen phthalate and hydrochloric acid the maximum buffer capacity is at about pH 2·8. A buffer of acetic acid and sodium acetate attains its maximum capacity in the region of pH 4·6. If the latter mixture is used to obtain pH 2·8 the buffer capacity is so small that it may no longer suffice to maintain a constant pH throughout the test.

Information on the stability of reactive dyeings is relevant to practical dyeing. Firstly, a reactive dye is suitable for bulk application only if the ratio of the rate of reaction with the fibre to the rate of saponification of the dyeing exceeds a certain minimum over a fairly wide range of fixing conditions. Secondly, there are several fastness tests which call for a high standard of alkaline stability, e.g. repeated severe washing tests with the addition of soda, and the test for soda-boiling fastness. For certain uses the resistance of the dyed fabric to acid hydrolysis is of decisive importance. It is not, however, possible to transfer directly the results of our examination to the behaviour of dyeings in these tests.

Mr. RAMSAY J. HANNAY (*President of the Society*) formally closed the Symposium by thanking, on behalf of the Society, all those who had worked to make the Symposium such an outstanding success.

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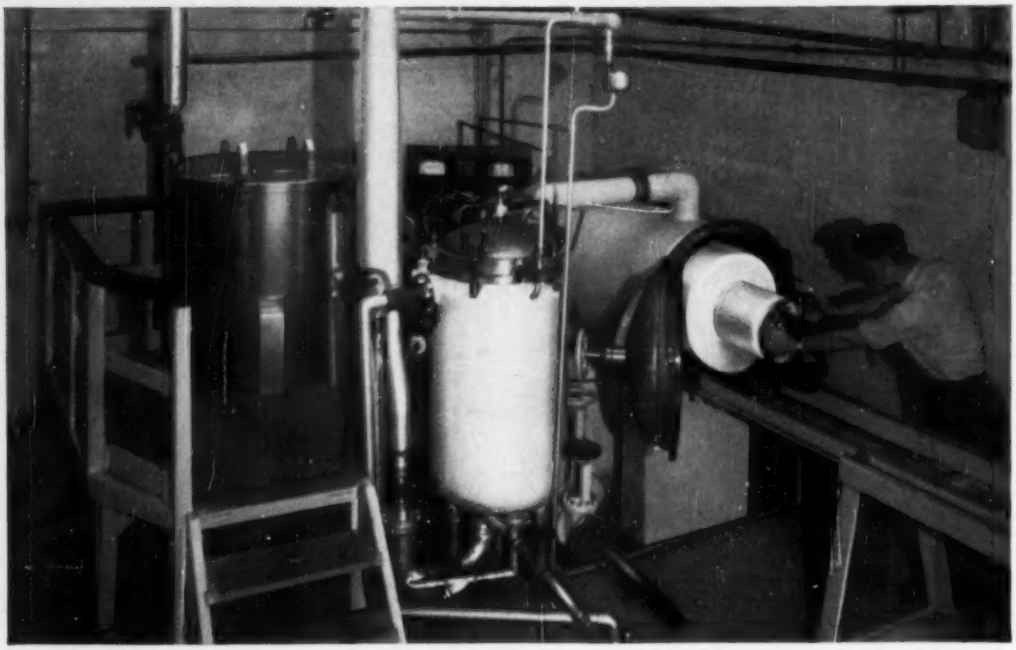

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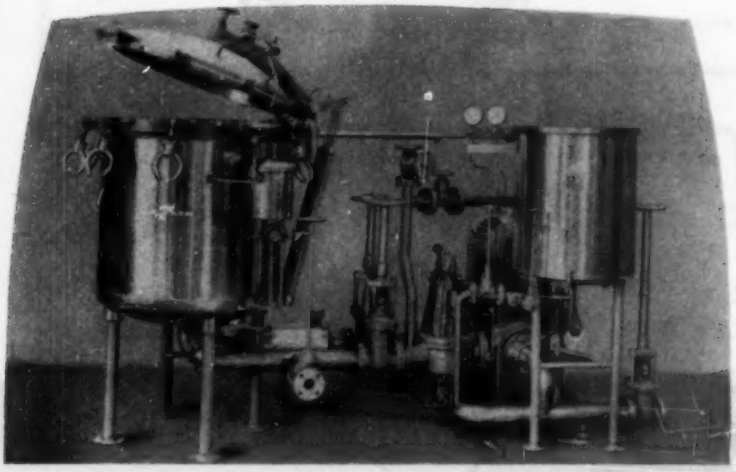

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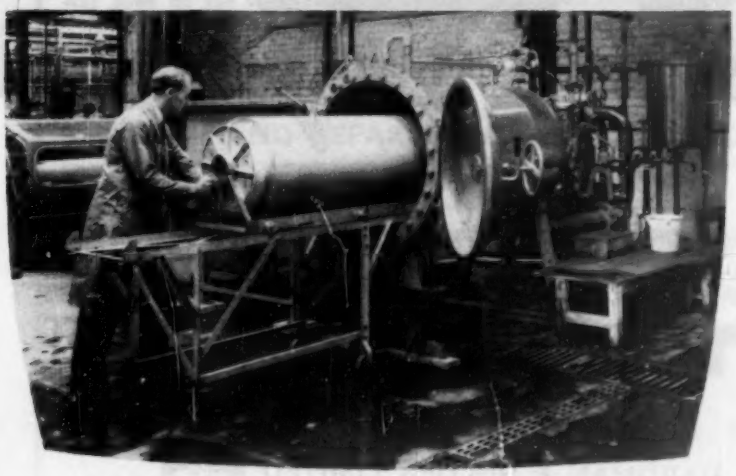

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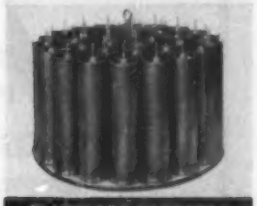

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